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THE EARLY HISTORY OF THE USE OF THE TERM LATERITE

J. A. PRESCOTT, F.R.S.

(*Waite Agricultural Research Institute, University of Adelaide*)

It will be recalled that the term *Laterite* was originated by Buchanan (1807) as the name for a surficial or shallow formation which he took at first to be an indurated clay and which was quarried and trimmed into the form of large bricks for building purposes in south India. Buchanan was a medical officer attached to the service of the East India Company and was associated with early explorations in Burma before being commissioned in 1800 to explore the territories of Mysore, Canara, and Malabar, which had recently been acquired by the Government of Madras. It was during this exploration that he first saw and named the material at Angadipuram (lat. 10° 58′ N., long. 76° 13′ E.).

In 1802–3 for a period of 14 months Buchanan lived at Katmandu in Nepal, and in addition spent some 2 years in the frontier districts of this State collecting information from travellers and refugees. He published a description of Nepal on the basis of the information so obtained (Hamilton, 1819), but there is nowhere in this account any mention of laterite.

From 1807 to 1814 Buchanan was commissioned to make a thorough study of certain districts in Bengal which are now comprised in Bihar, Bengal, and parts of Assam, and in 1814–15 and prior to his retirement to Scotland, where he adopted the name of Hamilton, in August 1816 he was superintendent of the Botanic Gardens in Calcutta.

The journals of Buchanan relating to the surveys in Bengal formed the basis of a descriptive publication by Martin (1838), and little of the original material was published at that time. The journal for Dinajpur appeared in 1833 as a supplement to *Gleanings in Science*, an early journal of the Asiatic Society of Bengal, and some notes on the minerals of the Rajmahal Hills from Buchanan's manuscript journals were published in this same journal in 1831.

The original journals for some of the districts were published, however, more than a hundred years later by the Government of Bihar, that for Patna and Gaya, edited by Jackson, in 1925, for Shahabad in 1926, and for Bhagalpur in 1930, both edited by Oldham.

A biographical notice of Buchanan was written by Prain (1905).

Buchanan did not use the term 'laterite' in these journals, but he used 'brickstone' and in several instances compared the local occurrences as at Bilkati, Jaipuri, and in the Rajmahal Hills with the 'brickstone of Malabar'. 'The brickstone', he remarked, 'seems to be composed of clay and red ochre of iron.'

An alternative term which was early introduced was 'iron-clay'. This was used by Voysey during his observations in central and southern India in 1818–24.

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It is evident from his notes that Voysey followed closely the mineralogical system of Werner which was the basis of the classification used by Jameson (1816) in dealing with the basalt family and comprising basalt, wacke, clinkstone, and iron-clay. Stirling (1825) gave the name Jamieson as the authority for the term 'iron-clay', evidently a misspelling for Jameson.

This term was included also as an alternative name for laterite in the first *Manual of the Geology of India* by Medlicott and Blanford (1879).

The first mention of laterite in formal scientific literature is that of Babington (1821), who dealt with the geology of the country between Tellicherry on the Malabar coast and Madras. He described the low hilly country below the western Ghauts and noted the hills to be composed of the 'ferruginous stone so peculiar to India, called by Buchanan laterite'. He described a quarry at Manantoddy on the old Madras road and the methods of quarrying, and depicted a two-lobed axe used for the purpose.

Stirling's reference is included in a comprehensive geographical and historical account of Orissa. He noted the occurrence of beds of laterite at the foot of the granite hills on the western margin of this district. His remarks are worthy of quotation.

> The rock most abounding in this division of the district next to the granite is that singular substance called Iron Clay by Jamieson, and Laterite by Dr. Buchanan. It lies in beds of considerable depth at the feet of the granite hills, often advancing out for a distance of ten or fifteen miles into the plains, where it forms gently swelling rocky elevations, but never rises into hills; sometimes it is disposed in the manner of flat terraces of considerable dimensions which look as if they had been constructed with much labour and skill. The composition and aspect of the Cuttack iron clay are very remarkable, from the innumerable pores and amygdaloidal cavities which it contains, filled with white and yellow lithomarge, and from the quantities of iron-ore pebbles and fragments of quartz imbedded in it.

The observations of Voysey were not published until many years after his death, while on duty, in April 1824. Two papers on his observations in Hyderabad were published in 1833, the second paper being merely a more orderly presentation of the first. Extracts of geological importance from some of his journals were published in 1844 and 1850.

It was Voysey who first encountered the laterite of Bidar so well described later by Newbold.

Voysey, as stated above, used the term 'iron clay' instead of laterite, but it is evident from his journals that he was familiar with the latter term and used it on at least three occasions in the last few weeks of his journal. At first he was inclined to consider iron clay as being confined to coastal regions or as extending only a short distance inland, and he was obviously also familiar with a 'not very dissimilar' formation at the Cape of Good Hope. His encounter with laterite at Bidar at an elevation of 2,000 ft., however, modified these views.

Calder (1833) made extensive use of Voysey's unpublished journals in his 'general observations on the geology of India', and also identified iron-clay with laterite.

A notable and useful contribution in this early period was that of Cole

(1836) of the Madras medical establishment, who brought together all the earlier references to laterite or iron-clay and related them to his own observations of the formation in the Red Hills near Madras. This paper was a deliberate effort to excite interest in an obscure subject, and his objectives are worthy of quotation.

> Now, that so little should be known concerning the *laterite*, a mineral so extensively distributed, and offering so peculiar a feature in . . . geology, constitutes an *opprobrium* to the science which it is desirable to efface; and I, therefore, propose to offer my imperfect observations on the position and character of the laterite, . . . prefaced by an account of what has been written hitherto on this remarkable rock, by way of inciting geological observers, to note down similar particulars, that so, by the accumulation of observations from various localities, some precise data may be arrived at, by which we may be enabled to assign its true geological position and history, to this singular mineral product.

Another member of the Madras medical service was Christie (1828, 1829), who prepared a series of papers on the natural history of the southern Mahratta country. He noted that 'the principal rocks of the peninsula of India are granite, transition rocks, old red sandstone, trap rocks, and superior to these, a ferruginous claystone'. He identified this clay-stone with the 'laterite of Buchanan' which 'covers large tracts both in India and the neighbouring countries'.

Christie illustrated his geological paper by means of a diagrammatic section across the Indian peninsula demonstrating the relationships of these rocks to each other. This paper and the section attracted the attention of Elie de Beaumont (1829), who was concerned at the time with the study of the origin of mountain ranges. He noted that the great fault with which appeared to be associated the escarpment of the western Ghauts and the elevation of the plateaux of the Mahratta country, the Deccan, and the Carnatic had elevated at the same time the great argillo-ferruginous deposit of laterite which formed the highest levels of these plateaux. He expressed a regret that this extensive deposit of laterite had not so far yielded any fossil and so could not be dated with certainty. Elie de Beaumont thus grasped quite early the association of laterite with uplifted peneplains which is so characteristic a feature of the formation.

Christie was again invited to Madras to examine the geology of the presidency, but he died there in November 1832 soon after his arrival.

At this period there was accumulating in India a considerable body of geological information, and much of this came to light with the establishment of the physical class of the Asiatic Society of Bengal. This Society had been founded in 1784, and its principal publication had been *Asiatic Researches*. Part 1 of vol. 18 (1833) was edited as the 'Transactions of the Physical Class' and included sixteen papers, most of which were of geological or mineralogical interest. This number had been preceded by three volumes of *Gleanings in Science*, published in the period 1829–31, and to which reference has already been made. A further journal belonging to this period was the *Madras Journal of Literature and Science*. Both these last named journals reproduced

papers and information from other sources including in 1836 that of Christie. It is essentially in this group of journals that the early information concerning laterite is to be sought.

Coneybeare (1835) had prepared a report on geological science for the British Association for 1831–2 in which mention is made of the work of residents in India and specific reference to the 'thin crust of laterite, a ferruginous clay considered as associated with the trap formation'.

Calder's paper (1833), mentioned above, belongs to this period. He dealt with the geographical distribution of laterite in India, and mentioned its occurrence on the shores of Sumatra and the Straits of Malacca and also in Ceylon. In dealing with the unpublished journals of Voysey he mentioned the latter's correspondence with Cullen in November 1820 in which Voysey had expressed an opinion on the possible origin of laterite. In Voysey's views 'the indurated clay . . . is very probably the result of those muddy eruptions so common, and of such extensive occurrence in South America. Indeed I am convinced that the greenstone, basalt, wacke, iron clay or laterite, and the indurated clay, have all a common origin, from the insensible degrees by which they pass the one into the other; and that they only differ as to the degree of pressure to which they have been subjected under fusion.'

This explanation of Voysey was noted by subsequent observers, but rejected relatively early.

Another original observer who had views on the origin of laterite was Everest (1833), who noted a 'hydrated iron ore' 30 miles north-east of Sagar which he believed to be the laterite of Buchanan. Everest (1831) had earlier inclined to the view that such ironstones could only be deposits from water.

Bird (1835), in a descriptive memoir of the country between Poona and Kittor, mentioned the occurrence of numerous pieces of iron ore and described certain undulating ground as composed of a 'red clay-ironstone or laterite' which was an aggregated rock used for building.

Benza (1836) in two separate papers dealt with the geology of the Nilgherry Hills and with the country between these hills and Madras. In these papers he discussed various occurrences of laterite both with respect to their characteristics and to their geographical distribution. He characterized laterite as a 'simple, compact, tubular or perforated ironstone', and expressed the opinion that 'the distinction of the different rocks included under the general term of *laterite*, ought to engage the labours, the researches and talents of geologists and chemists in India, to remove many doubts in Indian geognosy'.

A final reference may be made to what is probably the first attempt to map an area of laterite. This was by Jones (1833), described as 'an enterprising miner' who dealt with the coal measures of the Damodar valley and mapped the general spread of laterite along the eastern margin. This map may be compared with the very recent one of Kirk (1950) of the same district.

This early chapter of information concerning laterite may be said to close with the paper by Cole. The transition to the modern work of the Indian Geological Survey was through Newbold (1846).

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SOME SOIL-FORMING PROCESSES IN THE HUMID TROPICS

I. A FIELD STUDY OF A CATENA IN THE WEST AFRICAN FOREST

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WITH [redacted] PLATES

Introduction

In spite of considerable diversity in detail, the soils derived from igneous and metamorphic quartzose rocks, which extend over very large areas of the West African forest, have in common many essential and characteristic features. Many of the processes involved in their formation can only be revealed by intensive work on carefully selected soils—an approach to tropical soils that has been much neglected. The object of the present study was to reveal in detail the genesis of a catenary sequence of soils which showed the essential features of the soils of much of the West African forest and of many other parts of the world where conditions are similar.

In this first paper a field description of the catena is given, and the soil-forming processes revealed by this field study are discussed. This is intended to form a background to the detailed laboratory and supplementary field studies to be described later.

The main cause of differences among soil catenas in the forest of West Africa can be related to variations in the rocks from which they are derived. The rainfall, of from 50 to 150 in. over most of the forest, is sufficient to maintain thorough leaching of the soil, and gives rise to no marked change in the direction of soil-forming processes, although the soils under the higher rainfalls are in general more leached and more deeply weathered than those in the lower rainfall area studied. There is a dry season of from 3 to 6 months. The topography is usually undulating or rolling. The patterns of soil on each type of rock are related to the topography, and they provide excellent examples of Milne's (1935) catena of the first class.

The catenary sequence of soils in British West Africa was first recorded by Greenwood (1938), and descriptions of typical catenas of the extensive cocoa soils in the forest have been published by Vine (1941) and Charter (1949*a*). In this area any study of soil-forming processes must take the catena as its basis. A study of only the vertical development of a profile omits half the picture. The lateral relationships and variations between corresponding horizons in the catenary succession of profiles equally deserve study; and, as will be shown, it is impossible to understand the formation of the profiles on the lower parts of the slope unless the formation of the upper-slope members is understood, and the importance of such factors as lateral drainage and soil creep is appreciated. Greene

(1947) has emphasized the importance of lateral drainage in the development of the lower-slope soils of the tropics. There has been a tendency in the past to study only the freely draining soils of the upper slopes, and to neglect the less well-drained colluvial soils of the lower slopes, although they are of comparable agricultural and pedological interest.

The most important rocks of the forest are the granites, granodiorites, gneisses, and schists of the basement complex together with quartzite and schists of later age and unmetamorphosed sedimentaries. The soils most suitable for a preliminary study are derived from granites or gneisses because (*a*) they are primary; (*b*) they contain a wide range of mechanical size fractions which allows full play to processes such as illuviation, creep, and resorting by the soil fauna; and (*c*) their distribution is widespread through the tropics. The catena studied was developed from a gneiss at Ibadan, south-west Nigeria.

Physical Setting of the Catena

Geology. The parent rock was a banded granitic gneiss consisting of light-coloured bands of coarse-grained quartz and felspar up to 3 in. wide alternating with narrower fine-textured highly schistose dark-coloured bands of quartz, felspar, and biotite. Pockets of very coarse-textured pegmatite were common. This rock was deliberately selected because it was cut by numerous quartz veins up to 6 in. wide, running, as a rule, along the plane of foliation. These resist weathering and provide invaluable evidence of the junction between sedentary and transported horizons.

Physiography. The land form developed over the gneisses around Ibadan consists of an undulating plain, with an average altitude of 700 ft., draining towards the sea 70 miles to the south. The state of dissection is sub-mature, but the valleys are still young, without flood plains. Close to the streams there is often a slight increase in slope, suggesting that the rate of down-cutting has recently increased. The slopes then tend to rise smoothly at a constant gradient of around 5 per cent., and the general absence of a well-marked concavity at the footslope is notable. The upper parts of the slope are usually convex and meet to form smooth rounded divides, but at many points there are younger features and the slopes run with increasing gradient to the foot of small rocky outcrops.

The physiographic features of the catena studied were typical of the region, and in Fig. 1 the profile section of the valley studied is drawn to scale. The soil lay across the valley of the Alata stream immediately to the west of Ibadan airport. The whole drainage basin above the transect was underlain by the same rock, so that there is no doubt of the geological origin of the colluvial soils in the valley. Upslope from the slightly over-deepened valley, there were smooth straight slopes leading to rounded convex ridges, though in places the rocky outcrops, already mentioned, occurred on the summit of the divides. It is worth noting that there were no well-marked signs of more ancient peneplain surfaces in the district. The sites of the soil profiles investigated are indicated in Fig. 1.

Climate. The average annual rainfall at Ibadan is 48·4 in. There are two rainy seasons with maximum falls in June and September, a short relatively dry period in August, and a 4-month dry season from November to February. The average annual temperature is 80° F. with little variation in the monthly average. The relative humidity at midday averages 65 per cent. It is high during the rains (July, 78 per cent.) and low during the dry season (February, 49 per cent.).

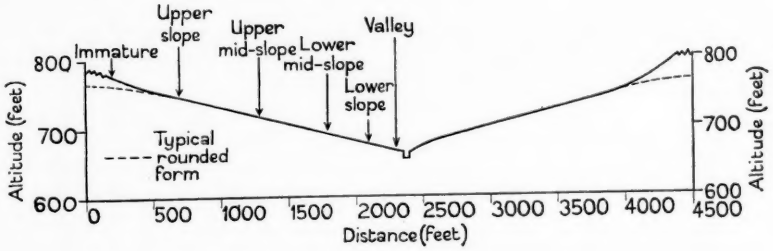


FIG. 1.

Vegetation. The natural vegetation is a type of high forest described by Keay (1949) as 'Dry Forest'. In this area the predominant species in the upper storey are *Chlorophora excelsa* Benth. and Hook, *Antiaris africana* Engl., *Sterculia oblonga* Mast., *Albizzia zygia* Macbride, and *Ficus* spp.; and in the lower storey *Randia maculata* D.C., *Diospyros* sp., *Lecaniodiscus* sp., and *Lindackeria* sp. may be mentioned. There is little variation in the composition of the forest with the soils of the catena except for the presence of characteristic riverain species in the immediate neighbourhood of the streams. Nearly the whole area has been farmed, and only isolated patches of secondary forest remain. Where the land has been heavily farmed it is dominated by spear grass, *Imperata cylindrica*, which is replaced in a few years by tall grasses, notably *Andropogon gayanus*. In less heavily farmed areas there is secondary bush in various stages of regeneration. The whole landscape is studded with oil palms. The rainfall is towards the lower limit needed to support high forest, and there are many parts of West Africa with a higher rainfall under savannah, but the determining factor is the severity of the dry season which at Ibadan is comparatively mild.

Description of the Catena

The essential features of the succession of profiles are shown diagrammatically* in Fig. 2, and the colour profiles in Plate I. In the descriptions which follow the terms defined in the U.S. Soil Survey Manual 1951 are adopted except that the international system of recording mechanical size fractions has been used. All colours are recorded for the moist soil.

* I am grateful to Mr. C. F. Charter for introducing me to this form of representation.

Immature
Upper slope
Upper mid-slope
Lower mid-slope
Lower slope
Valley
Oxid
Oxid-red
Red
Cr W
Cr T
Cr G
S
in.0
12
24
36
48
60
72
84
96
108
120
132
144
Sand
Fine sand
Clay
Mottling
Quartz gravel
Iron concretions
Manganese concretions
Iron pan
Rock
Decomposed rock
Cr W, worm-formed horizon
Cr T, termite-formed horizon
Cr G, horizon of gravel accumulation
S, sedentary horizon

FIG. 2.

1. *Immature profile*

Vegetation: tall grasses, notably *Andropogon gayanus*.

Cr W and Cr T	0–4 in.	Dark reddish-brown loose humic loamy sand; disturbed; 1–6 in. thick; changing clearly to
Cr G	4–30 in.	Reddish-brown, changing to red, stony gravelly sandy clay loam, changing from friable to compact. Residual gneiss stones, and quartz and concretionary gravel; 15–30 in. thick; changing gradually to
S_2	30–36 in.	Red compact sandy clay loam, containing small soft yellowish-brown and red mottled pieces of decomposed gneiss; 6–12 in. thick; changing diffusely to
S_3	36–66 in.	Decomposing gneiss showing yellow, brown, and red colours; 12–48 in. thick; changing diffusely to
	66+ in.	Fairly fresh gneiss.

2. *Upper-slope profile*

Vegetation: Imperata cylindrica.

		Sparse leaf litter.
Cr W	0–1 in.	Dark reddish-brown (5 YR 3/2) humic fine sandy loam containing fragments of worm casts and many fine roots; weak fine crumb structure; ½–1 in. thick; changing sharply to
Cr T	1–10 in.	Dark reddish-brown (5 YR 3/3) loose loamy coarse sand with many roots; 4–12 in. thick; changing gradually to
Cr G	10–27 in.	Reddish-brown (5 YR 4/3) gravelly coarse sandy loam changing to gravelly coarse sandy clay loam; slightly compact changing to compact; structureless; the gravel is mainly angular to sub-angular quartz with subsidiary hard iron concretions, and a few soft black concretions containing manganese oxides; 12–30 in. thick; changing gradually to
S_1	27–54 in.	Red (2·5 YR 4/6) compact sandy clay; a few small pisolitic iron and soft manganese concretions; structureless; moderate roots; 12–36 in. thick; changing diffusely to the *oxidation-reduction zone.*
S_2	54–72+ in.	Yellowish-red (5 YR 4/6) mottled light grey (2·5 Y 7/2) and red (lesser) compact sandy clay containing many small soft yellowish-brown and red mottled residual fragments of decomposing gneiss sometimes showing slight black manganese-oxide staining; structureless; few roots.

The soil series of which this profile is representative has now been named the Iwo series (H. Vine, private communication).

The horizons of the profile on the summit of the rounded ridges are in general slightly shallower but fall within the limits given above.

3. *Upper mid-slope profile*

Vegetation: forest regrowth about 20 years old.

		Thin broad-leaf litter.
Cr W	0–1 in.	Dark reddish-brown (5 YR 3/2) fine sandy loam; weak fine crumb structure; ½–1 in. thick; changing sharply to
Cr T	1–24 in.	Dark reddish-brown (5 YR 3/4) loose loamy coarse sand; moderate roots; 15–24 in. thick; changing gradually to

Cr G	24–48 in.	Red (2·5 YR 4/6) compact gravelly coarse sandy loam; structureless; few roots; the gravel is of angular to sub-angular quartz and soft to hard manganese concretions up to 1 in. diameter surrounded by a thin ferruginous shell; little pisolitic iron gravel; 24–36 in. thick; changing diffusely to the *oxidation-reduction zone.*
S_1	48–96+ in.	Yellowish-red (5 YR 5/6), mottled light grey, (increasing) red (10 R 5/8) and reddish-yellow, sandy loam; more compact than above; some soft black manganese concretions up to ½ in. diameter.

4. *Lower mid-slope profile*

Vegetation: Imperata cylindrica.

Very sparse litter.

Cr W	0–1 in.	Dark greyish-brown (10 YR 4/2) humic fine sandy loam; weak fine crumb structure; many fine roots and worm-cast fragments; ½–1 in. thick; changing sharply to
Cr T	1–18 in.	Dark reddish-grey (5 YR 4/2) changing to reddish-brown (5 YR 4/3) loose coarse sand; many, changing to few, roots; 15–24 in. thick; changing clearly to
Cr G_1	18–48 in.	Reddish-brown (5 YR 4/4) gravelly coarse sandy loam containing many soft black manganese concretions up to ½ in. diameter usually surrounded by a thin soft yellowish-red iron band, and a little quartz; structureless; changing diffusely to the *oxidation-reduction zone.*
Cr G_2	48–94 in.	Brown (7·5 YR 4/4) with red, reddish-yellow, and diffuse grey mottle, compact gravelly sandy loam; structureless; very few roots; gravel as above, but quartz increases notably towards the base; changing abruptly to the *reduced zone.*
S_2	94–108+ in.	Pale yellow (5 Y 7/3) sticky silty clay containing strong brown (7·5 YR 5/6) patches of highly decomposed gneiss.

Water seeped into the pit below 94 in.

5. *Lower-slope profile*

Vegetation: Imperata cylindrica; recently farmed.

Cr W and Cr T	0–18 in.	Very dark grey-brown (10 YR 3/2) changing to brown (7·5 YR 5/4) loose sand; moderate roots; surface 6 in. disturbed by recent cultivation; 15–24 in. thick; changing clearly to
Cr G_1	18–30 in.	Strong brown (7·5 YR 5/6) loose gravelly sand; moderate roots; the gravel consists of weathered iron concretions with friable yellowish-brown interior and harder dusky red exterior, and some soft black manganese concretions and a little quartz; changing abruptly to the *oxidation-reduction zone.*
Cr G_2	30–48 in.	Iron pan consisting of irregular iron-rich knobbles up to 1 in. diameter diffusely mottled white, yellow, brown, black (manganese), and dusky red (10 R 3/2) in a hard ferruginous strong brown (7·5 YR 5/8) matrix. The pan breaks fairly easily between knobbles, but these are strongly cemented particularly in their dusky red portions which tend to surround the outside of the knobble. The matrix is permeated with small channels loosely filled by pale brown coarse sand. A few soft manganese dioxide concretions; changing diffusely to

Cr G_3	48–84 in.	Strong brown (7·5 YR 5/8) compact fine gravelly coarse sandy loam containing weakly cemented, changing to uncemented, mottled iron-rich pockets. A little quartz gravel. This horizon is essentially the same as the one above but is less cemented and contains no channels; changing clearly to the *reduced zone.*
Cr G_4	84–90 in.	Light brownish-grey (2·5 Y 6/2), mottled brownish-yellow, sticky gravelly clay loam; more quartz gravel than above; soft iron concretions and very soft large black manganese oxide concretions; changing clearly to
S_1	90–102 in.	Light olive-grey (5 Y 6/2), faintly and diffusely mottled light yellowish-brown sticky clay loam; changing gradually to
S_2	102–20+ in.	Very pale brown decomposing pegmatite, the upper portion being penetrated by tongues of clay as horizon above.

6. *Valley profile*

Vegetation: Imperata cylindrica.

		Very thin litter.
Cr W and Cr T	0–24 in.	Dark grey (10 YR 4/1) changing through grey-brown (10 YR 5/2) to light yellow-brown (10 YR 6/4) loose coarse sand; the surface 6 in. recently disturbed by cultivation; many changing to few roots; changing clearly to
Cr G_1	24–36 in.	As above but a little coarse angular to sub-angular quartz gravel; changing gradually to the *oxidation-reduction zone.*
Cr G_2	36–48 in.	Light yellowish-brown (10 YR 6/4) changing to brownish-yellow (10 YR 6/6) slightly mottled yellowish-red and brown, slightly gravelly coarse sandy loam; slightly compact; some soft black manganese oxide concretions surrounded by a thin yellowish-brown iron band; changing gradually to the *reduced zone.*
Cr G_3	48–108 in.	Blue-green slightly sticky sandy clay loam; changing to sandy loam below 84 in., with coarse distinct yellowish-brown mottle; a little angular to sub-angular quartz gravel increasing to a marked stone line from 96 to 108 in.
S	108–44+ in.	Mainly dark grey-brown (2·5 Y 4/2) decomposing biotite rich gneiss. There are horizontal bands about 2 in. wide of blue-green more highly decomposed gneiss at 120 and 132 in. A quartz vein 2 in. wide running nearly vertically ceased abruptly at the stone line above.

Water was seeping into the pit below 42 in. at the end of the dry season, but the seepage was slow enough for digging with the aid of a bucket.

Discussion

The main horizons

There are two primary genetic horizons in each of these profiles. They are:

Cr—the horizon of soil creep,
S—the sedentary horizon.

The Cr horizon is further subdivided into three quite distinct genetic horizons.

Cr W—the horizon formed from worm-cast material,
Cr T—the horizon formed largely by termites,
Cr G—the horizon of gravel accumulation.

These genetic horizons cut right across and dominate the divisions that could be made based on the customary A, B, and C horizons. This lettering is justified, as are the letters A, B, and C in other profiles, by the shorthand information they give about the genesis of the profiles. The difficulties of the A, B, and C terminology will be discussed later.

The S horizon has been divided into the S_1 horizon with little decomposed rock visible, the S_2 horizon with many decomposed rock fragments, and the S_3 horizon which is altered rock retaining the structure of the fresh rock.

The evidence for the genetic divisions may best be introduced by a consideration of the development of the mature upper-slope profile.

The upper-slope profile

The lowest horizon S_2 (54–72+ in.) contains abundant traces of the structure of the parent gneiss, which has decomposed leaving some of its primary minerals and secondary pseudomorphs orientated in the original plane of foliation. In an extended section, quartz veins, resistant to weathering, may be seen cutting across this horizon in the plane of foliation. They are usually fissured into potential gravel fragments but are otherwise undisturbed. Plate II (*a*) shows such a vein exposed in a railway-cutting that crosses the head of the drainage basin studied.

In horizon S_1 above (27–54 in.), the traces of altered rock have nearly disappeared to leave a red sandy clay; but wherever quartz veins occur, they show that the soil is still *in situ*. The horizon contains a little concretionary iron gravel which is formed by the secondary deposition and hardening of iron oxide in small residual fragments of decomposed rock.

At the top of this horizon there is a well-marked change to the Cr G horizon containing abundant quartz and concretionary iron gravel. The quartz gravel is clearly derived from the quartz veins, which may be seen to bend over in the transition between the S_1 and Cr G horizons and disintegrate into a series of fragments at the base of the Cr G horizon, an effect well shown in the railway-cutting mentioned above, see Plate II (*b*). As will be proved later, the quartz gravel is concentrated in this horizon by eluviation of clay, further decomposition of the silt and sand fractions, and removal by termites of fine earth fractions into the horizon above, where they are moved more rapidly by creep. It has been found that there is twice as much quartz and concretionary gravel in this horizon as would be expected from the concentration of quartz veins and concretionary gravel in the S_1 horizon.

When the nature of the parent rock or its veins is such that fragments resistant to weathering may persist in the upper layers of the soil, a band of gravel and stones is invariably formed over the sedentary soil horizons, and is a common sight in road and railway-cuttings in West Africa. The

most important rocks concerned are granites, gneisses, schists, and quartzites. Concretionary iron gravel will also accumulate if it is formed, or begins to be formed, in the upper part of the sedentary or the gravel horizon. However, it is not such a useful guide to the junction of the sedentary and creep horizons as quartz gravel, because it is scattered in the upper part of the sedentary horizon, whereas the quartz occurs as distinct veins.

The importance of soil creep on soils with slopes of as little as 5 per cent. has been little recognized by pedologists. It seems likely that many apparently sedentary profiles have their top soils derived not from material directly below but from the subsoil higher up the slope.

Above the Cr G horizon there is a fairly sharp transition to the Cr T horizon of gravel-free loamy coarse sand about 6 in. thick. Except in the most severely eroded areas where the gravel horizon is exposed on the surface, this layer of gravel-free soil is an invariable feature of West African soils. Doyne and Watson (1933) suggest this horizon 'may be detritus from another source, or more probably may be due to a secondary weathering of the concretion layer itself', and Vine (1941, loc. cit.) has suggested it is due to earthworms. Charter (1949*b*), discussing the principal cocoa soils of the world, has described the characteristic upland soils of the tropics as three-layered soils which, over granodiorite in the Gold Coast as an example, consist of a lower layer of mottled gritty clay merging into disintegrated granodiorite, an intermediate layer of sandy clay in which gravel is accumulated, and a sandy upper layer; and he goes on to say that the gravel would accumulate on the surface but for the activity of numerous soil animals which bring fine earth to the surface.

There are certainly special areas, notably beneath scarps, and on some lower slopes in undulating country, where gravel-free horizons may be ascribed to soil wash or detritus, and in northern Nigeria there is wind-blown material several feet thick covering gravel (Vine, 1949); but the general occurrence of the phenomenon, and the close relation between the size and nature of the sand in the gravel-free top soil and in the subsoil, preclude such explanations as a general rule south of the dry Sudanese zone. If iron gravel alone was present in the Cr G horizon the gravel-free horizon above might well be due to 'weathering of the concretion layer itself', as described by Carroll and Jones (1947) in south-western Australia for the sandy uppermost horizon overlying massive laterite; but the general absence of quartz gravel as well as concretionary gravel in the gravel-free horizon shows this cannot be accepted as an explanation for the soils under discussion. There can be little doubt that, in general, the horizon is formed by the soil fauna which bring up fine earth, leaving behind those particles too large for them to carry or digest. The activities of the fauna in the area studied will be described in some detail later; and it will be shown that termites are mainly responsible for the Cr T horizon, there being a sharp limit to the maximum size of particle in this horizon at 4 mm., which corresponds to the maximum size of particle in the mound of the principal and largest termite, *Macrotermes nigeriensis*. Were it not for this activity the Cr G horizon would be exposed on the surface; and as the gravel content is often over

50 per cent., this process is clearly very important to agriculture. Since Shaler (1891) measured the large amounts of earth brought to the surface by ants at Cambridge, Massachusetts, there appears to have been no further work on this important activity of termites and ants.

Finally, the uppermost Cr W horizon (0–1 in.) of fine sandy loam consists mainly of humus and breakdown material from the worm casts of *Hippopera nigeriae* which abound over the surface of the soil in this area. The mineral matter of the worm casts is derived from earth near the surface, so that the worms, in sorting fine material from the Cr T horizon and voiding it on the surface, are acting in the same way towards this horizon as the termites are towards the Cr G and S_1 horizons. Although earthworms are widespread in the West African forest they are specially abundant round Ibadan, where the Cr W horizon is particularly noticeable. Plate III shows the casts left on the surface at the end of the rainy season.

Catenary development of the main horizons

The changes that occur in these characteristic horizons according to the position of the profile on the slope may now be described.

Thickness of horizons

In the Immature Profile, at the top of the slope beneath a rocky outcrop, the nearly fresh rock is exposed at a depth of 5 ft. Below the Cr G horizon there is only the S_2 horizon, for the gneiss has not decomposed sufficiently to give the S_1 horizon of concolorous red sandy clay with few decomposed fragments. The Cr G horizon varies in thickness between the same limits as in the upper slope profile; but it contains, in addition to quartz and concretionary gravel, much decomposing rock derived from fragments which have broken off from the outcrop at the summit about 50 yards away, and have been transported by creep. It will be noted that these fragments have almost entirely disappeared in the upper slope profile some 160 yards farther down the hill. It is an interesting fact that there are relatively few gneissose fragments smaller than stones over 6 in. long.* This suggests the fragments break off along joints, and the resulting stones are then decomposed chemically throughout their mass, retaining their shape until they finally crumble. The Cr T horizon is usually a little shallower than that of the upper-slope profile. The Cr W horizon, when it is undisturbed, is always from $\frac{1}{2}$ to 1 in. thick at all points on the slope.

In the upper mid-slope profile the Cr T horizon has increased from about 6 in. to 24 in. in thickness. This is to be expected, for so long as the termites are active all the way down the slope, under equilibrium conditions each successive section across the slope must pass by creep not only the material passed down from the section above but also any additional material brought up by termites in the section. As the slope is uniform and the differences in the rate of creep of the layer below will be small, the thickness of the Cr T horizon must increase progressively. The Cr G horizon has also increased slightly in thickness from about

* I am obliged to Mr. J. C. Pugh for calling my attention to this fact.

15 to 27 in., probably for the same reason that the Cr T horizon has increased, for material is constantly being added to this layer from the upper part of the S_1 horizon below.

In the lower mid-slope profile the Cr T horizon is no thicker and it remains at about the same thickness down to the valley, which suggests the amount of material being carried from below 24 in. is balanced by remixing at the junction of the Cr T and Cr G horizons. The Cr G horizon, however, has increased to a thickness of 6 ft., and within the horizon the quartz gravel tends to increase towards the base. In the lower slope and valley profiles there is little further change in the thickness of this horizon, but within it, the quartz is progressively more concentrated towards the base, and in the valley profile it appears as a marked stone line.

Colour and drainage

For further discussion of the elements of this catena the drainage pattern must be described. On the rock exposures themselves most of the rain runs off and is absorbed by the soil abutting the flanks. On the well-drained upper slopes the rainfall drains vertically through the profile: the permeability of the very friable humic top soil overlying loose loamy coarse sand is very high, and even the heaviest rains are absorbed without run-off. The red earth below, in spite of a clay content of up to 40 per cent., is very permeable, and the downward percolation of the water is not checked until fairly fresh rock is reached, which has been found in a pit at a depth of 28 ft. Here there is a perched water body, and the water soaks laterally over the surface of the slightly decomposed rock. The main ground-water table is in the joints and fissures of the undecomposed rock and is probably many feet below (to be discussed in Part II). At the bottom of the pit there was a slow seepage of water in February, and the water-level was the same in July, so that there is no question of ground water influencing the present development of the upper-slope profile described.

In the upper mid-slope profile the subsoil colours are similar to those of the upper slope profile and only increasing manganese oxide concretions in the S_1 horizon below 4 ft. suggest moister conditions. In the lower mid-slope profile the influence of water draining from higher ground is first noticed. Here the predominant colours from 18 to 94 in. have brown instead of red hues, and there are many manganese oxide concretions (see Plate I). Below 48 in. traces of iron oxide are deposited but not sufficient to cement the soil. At 94 in., corresponding to the junction of the Cr G and S horizon, there is seepage and a sharp change to a grey 'reduced' colour.

In the lower-slope profile the reduced zone is met at 84 in., in this case in the lower part of the gravel horizon. The soil is enriched with iron oxide below 30 in. and the upper part of this zone, which has the opportunity to dry out thoroughly in the dry season, is hardened to form a pan. At an occasional spring line near the stream flocs of yellow-brown ferric hydroxide are even deposited on the surface.

Finally, in the valley profile, seepage occurred at many points in the

Cr G horizon and filled the pit to within 42 in. of the surface at the end of the dry season; and the soil colour below this point is bluey green. The area was not flooded during the rains, and there were no levees on the stream bank.

Texture

Within each profile there are marked variations in texture (see Fig. 2). In the upper-slope profile the clay content increases rapidly from the Cr T horizon, which is a loose loamy sand, to the top of the S_1 horizon, which is a compact sandy clay, and it then decreases very gradually. The immature profile also shows its maximum clay content at the top of the S horizon. In the upper mid-slope profile the point of maximum clay is met at about the same depth, 24 in., but this is now in the Cr G horizon. In the lower mid-slope profile with its deep Cr G horizon the distribution of clay is different: the content rises as usual to a depth of 24 in., but throughout the Cr G horizon to 94 in. there is little change. Here, at the water-table, there is a very sharp boundary, below which is a marked accumulation of illuvial clay washed into the well decomposed rock. In the lower-slope profile there are the same changes, and in this case, below the accumulation of illuvial clay 18 in. thick at the base of the profile, tongues of illuvial clay could be seen penetrating the underlying decomposed pegmatite. In the valley profile clay has been eluviated from the Cr T and also the top of the Cr G horizon, so that there is about 3 ft. of loose coarse sand above the usual sandy loam of the Cr G horizon. There is another fairly sharp increase in illuvial clay at the top of the reduced zone; the sandy clay loam thus formed extends from 48 to 84 in. below which the clay content declines, and little clay has been washed into the decomposed gneiss below 108 in.

This marked loss of clay in the surface horizons of soils developed over rocks which contain coarse quartz grains is a regular feature of tropical and sub-tropical soil profiles, and its mechanism may be considered here. Both vertical and lateral eluviation are possible. Lateral eluviation of clay by surface or sub-surface run-off has been noted by many observers. Robinson (1936) has suggested that the rather more sandy texture of the surface soils on the English Gault clay is caused by removal of clay along the surface or along the surface of the water-table; and Milne (1936), describing a catena near Lake Victoria somewhat similar to the one studied here, writes: 'Storm water running over the surface is gradually paring off the top soil, and the spoil travels differentially according to particle size, so that by cumulative effect a zone of washed sand covers the footslope below, silty or clayey sand lies beyond it, and a level clay floor fills the bottom land'; finally Charter (1949*b*), describing cocoa soils, has stated that 'the sandy upper layer owes its origin to rain-water draining laterally through the surface and carrying with it the clay—tropical rainfall being on the whole too heavy to allow all the water entering the soil to percolate downwards so that some has to find its way into streams as sub-surface flow'. In many places a sub-surface flow of storm water through the gravel horizon above the more compact S horizon may be seen in cuttings. It was, however, observed

in the present case that even during the heaviest storms there was no surface run-off from land covered by savannah grass or forest, nor could any sub-surface flow be seen at the sides of pits; all water in fact appeared to be draining vertically.

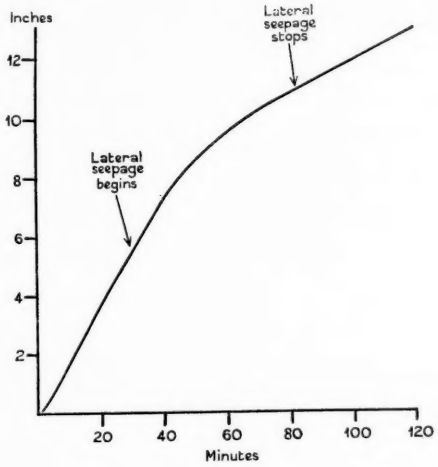


FIG. 3.

As a check on these observations the following rough percolation experiment was carried out. A plot, 6 ft. × 6 ft., was marked out close to the upper-slope profile. It was under a moderate growth of *Imperata cylindrica*. A long trench was dug on the down-slope side of the plot, to leave a strip 1 ft. wide between the bottom edge of the plot and the edge of the trench. The experiment was carried out in early July, the middle of the rains, and heavy rain had fallen the previous day, so that the soil was already very moist. The boundary strip was first saturated with water from a watering can. Water was then sprinkled on the plot from the can, held at a height of 5 ft., at such a rate that the surface was just able to absorb all the water without any run-off. Meanwhile a watch was kept for lateral sub-surface flow into the side of the pit. The rate of infiltration is shown in Fig. 3. In the first 30 minutes the soil absorbed water at the rate of 11·2 in. per hour, in the next 30 minutes at 7·8 in. per hour, and in the second hour at 3·25 in. per hour. Seepage into the pit did not begin for 28 minutes when the soil had received 5·2 in., and it developed at a depth of 27 in. corresponding to the boundary between the S and Cr G horizons and near the point of maximum clay content. The seepage did not develop above a depth of 24 in., and when the rate of absorption at the surface dropped to 3·25 in. per hour it ceased altogether. The experiment thus confirms that this very porous soil is well able to absorb the most intense rainfall without run-off, and that there is no lateral sub-surface flow. Eluviation of the clay must therefore be almost entirely vertical.

The illuvial clay deposited is at a maximum at about 2 ft., but, as will be shown in the next paper, decreases only gradually in amount, and there are traces down root channels to 16 ft. in the upper-slope profile. All this illuvial clay has not been derived from the eluvial layer above. The profile must rather be seen as in a continuous state of development in which the upper horizons are being removed by creep and constantly renewed by material from the top of the sedentary horizon, while at the same time, and keeping pace with this development, a mass of clay is being washed down the profile through the fabric of decomposed rock.

It will be noted that Milne, in the passage quoted above, has explained the washed sand at the foot slope as being due to the paring off of the surface and differential travel of the spoil, whereas in the present case the accumulation of loose sand at the top of the lower slope and valley profile is the result of a combination of creep and vertical eluviation of clay. This difference depends on the change from marked lateral surface drainage to entirely vertical drainage.

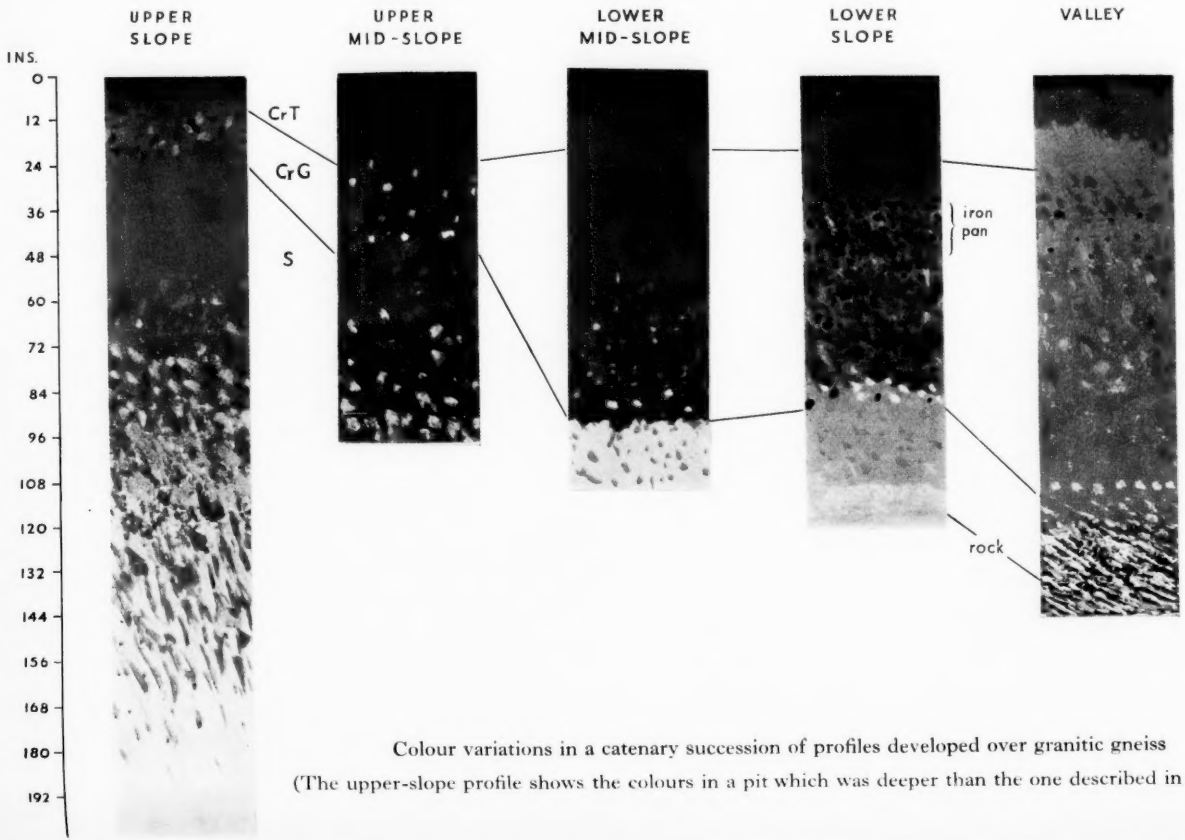
The difficulty of applying the customary A, B, C horizon nomenclature to these soils may now be seen. The junction between the A and B horizons changes from the top of the S horizon in the upper slope to the top of the Cr G horizon in the lower slopes. The Cr W horizon, richer in clay than the Cr T horizon, is an anomaly in the A horizon. The boundary between the B and C horizons is indefinite and lies between about 4 ft. and about 10 ft. in the upper-slope profile, and in the lower-slope profiles cannot be identified at all above the gley horizon at about 8 ft.

Consistence and structure

In all profiles the Cr W horizon is very friable with a weak crumb structure and the Cr T horizon is loose and has a single grain structure. The Cr G horizon is slightly compact and the S_1 horizon is compact. Both have been described as structureless. Not even fine cracks can be seen on the well-dried faces of the upper-slope profile, and although a mass of soil, if removed, will break down under slight pressure into smaller and smaller sub-angular blocks it is not considered that these are true peds.

Summary

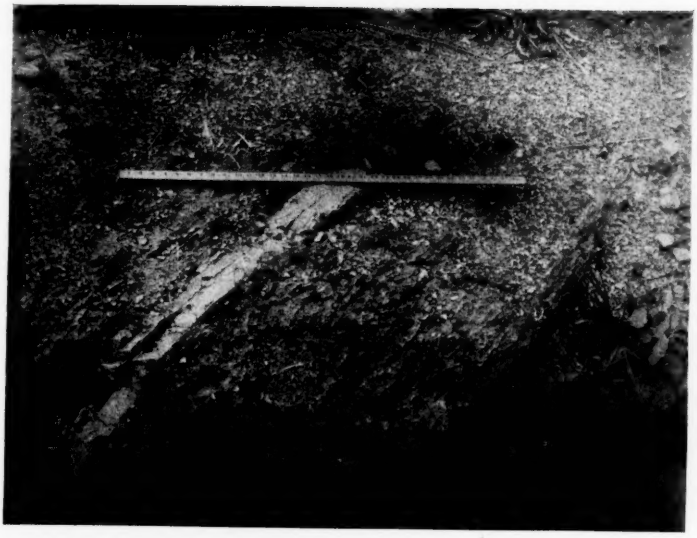
A field study of the formation of a typical catena developed over banded biotite gneiss in the forest region of West Africa has been made. In all profiles there are shown to be two main genetic horizons—a sedentary horizon and an horizon of soil creep above. The latter is divided further into an upper horizon formed by worms, an intermediate horizon formed by termites, and a lower horizon of gravel accumulation. The development of these horizons on the mature upper-slope member is first explained, and then their progressive development down the slope. The drainage pattern and the lateral and vertical changes in colour, texture, structure, and consistence are discussed. The paper forms a background to detailed laboratory and supplementary field studies to be described later.



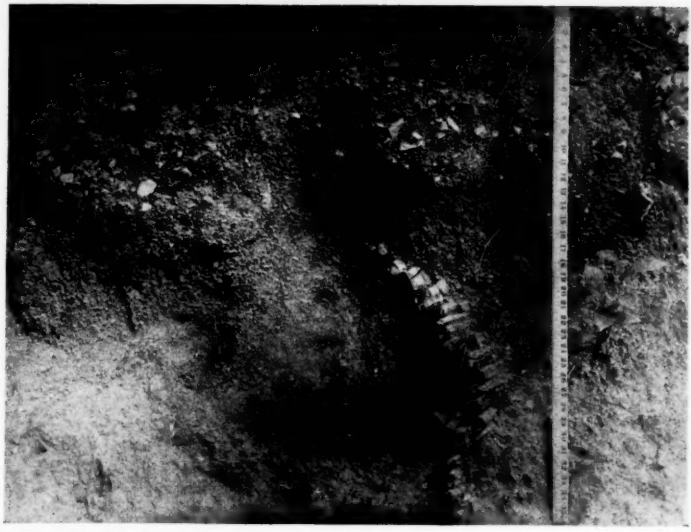
P. H. NYE—PLATE I

Colour variations in a catenary succession of profiles developed over granitic gneiss

(The upper-slope profile shows the colours in a pit which was deeper than the one described in the text)



a



b

a. Quartz vein in decomposing gneiss
b. Quartz vein showing creep

P. H. NYE—TROPICAL SOIL-FORMING PROCESSES—PLATE II

Worm casts left on soil surface after the rainy season

P. H. NYE—TROPICAL SOIL-FORMING PROCESSES—PLATE III

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THE RELATIONSHIP OF SOILS AND FOREST GROWTH IN THE ALGOMA DISTRICT OF ONTARIO, CANADA

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WITH ONE PLATE

DURING the summer of 1952 the authors made a general survey of soils, ground water, and forest cover on an area of approximately 250,000 acres, located in northern Ontario, at the intersection of the Algoma–Hudson Bay and Canadian National Railways. This area comprises level or undulating fluvio-glacial and lacustrine deposits interrupted in places by rock outcrops and rugged ridges of terminal moraines.

The extremely cold and humid climate owes its characteristics to the proximity of Hudson Bay, located at a distance of 150 miles. The average annual temperature is 35° F. The average temperature of the growing season, 63° F., is only 12° above the minimum established by Mayr (1909) for the timber line. The growing season is confined to June, July, and August, but even these months are not free from occasional frosts. The mean winter temperature is often close to 0° F. The annual precipitation approaches 30 in., nearly two-thirds of the rain falling during the summer months.

The low rate of evaporation and abundant rainfall give rise to the wide occurrence of hydromorphic soils (Hills, 1944) which are underlain by ground water at a depth of less than 4 ft. and dominate both the elevations and depressions. Otherwise, the soils of this region are strongly modified by the process of podzolization which is active in non-calcareous as well as lime-bearing substrata.

From the standpoint of management, the forests of the Algoma district have one serious disadvantage—their inaccessibility. This is primarily caused by extensive muskegs and shallow gley soils—natural obstacles to the construction of hard-surfaced roads. Outside of the winter months, transportation is limited to motor-driven speeders on narrow-gauge tracks, canoes on a few sluggish streams, and slow, exhausting marches by foot. A low fire-hazard and the enormous capacity of all soils for natural regeneration are among the positive aspects of the region. In spite of the clear-cut deforestation at the end of the last century, the forests in this part of Ontario form today an immense, uncharted green sea, extending for hundreds of miles.

The work of the writers was greatly facilitated by the forestry personnel of the Newaygo Timber Company, who had previously made use of aerial photographs and had accomplished many strip surveys in the remote parts of the region. These experiences served as an invaluable guide in the location of representative plots of different soil-forest units. The cruising records from the same source provided most of the information on the timber yields.

Method of Study

The determination of the composition and site indexes of forest stands was made on 2-acre plots by generally used mensuration techniques. Particular attention was given to quantitative analysis of the ground-cover vegetation, performed by a chain transect method (Wilde, 1951*a*). This method evaluates floristic associations on a basis of the following aspects: *tally* (T), the number of plants of a certain species encountered on a linear transect in a distance of 100 ft.; *frequency* (F), the number of 10-ft. segments in which a species occurs in relation to the total number of 10-ft. segments surveyed, expressed on a percentage basis; *coverage* (C), percentage of the total chain length occupied by the consolidated growth of a species. As far as conditions permitted, the *probable occurrence* of species in different soil-forest units, on a percentage basis, and *ecological amplitudes* of species were also considered.

The study of soils in the field consisted of excavation of trenches, descriptions of soil profiles, and collection of samples. The identification of the nature of soil was facilitated by the use of rapid tests for soil permeability, texture, organic matter, reaction, and content of free carbonates. In hydromorphic soils, these tests were supplemented by analyses of ground water, including potentiometric determination of pH value and redox potential, specific conductance by means of a resistance bridge, and content of dissolved oxygen by a modified Winkler method (Wilde, 1946 and 1950; Pierce, 1953; A.P.H.A., 1946).

The laboratory analyses of soil samples were made by the following methods: reaction electrometrically, using a glass electrode; exchange capacity and exchangeable bases by leaching with 1 N ammonium acetate and subsequent titration and spectrophotometric readings; total nitrogen by the Kjeldahl method; total carbon by electric furnace combustion and titration; available phosphorus by a stannous chloride-molybdate method; available potassium—spectrometrically; texture by a hydrometer method; free carbonates by means of an aneroid calcimeter; and specific conductance on 1:2 suspensions by a Solu bridge provided with a cathode-ray tube (A.O.A.C., 1950; Attoe and Truog, 1945; Bouyoucos, 1936; Chapman and Kelly, 1930; Kolterman, 1952; Lafond, 1950; Peech, 1947; Truog, 1930; Wilde, 1951*b*).

The observations in the field revealed that the Algoma region is strongly influenced by two types of plant succession. One, the general succession, caused by the geological youthfulness of the area, and particularly prominent on hydromorphic soils. Another, the local succession, caused by fires and man's activity, and reflected in the general tendency of the displaced climax forest to regain its temporarily lost ground. Because of these trends it is not uncommon that an essentially similar substratum is occupied by two or sometimes three phases of the same successional catena, for example: a brush cover of alder and willows; a pioneer stand of aspen, paper birch, and balsam poplar; and a climax forest of black spruce with an understorey of balsam fir.

These successional trends and the topographic modifications of the soil profile give rise to a large number of morphological varieties or

'types', the description of which is beyond the scope of this paper. The broad soil-forest units, which are in the key positions of different catenas and which are characterized by more or less complete successional cycles, are as follows:

a. *Skeletal soils*, including rock outcrops and boulder pavements. These are occupied by slowly growing stands of jack pine, black spruce, and paper birch with ground cover of lichens, mosses, and blueberries.

b. *Sandy podzols* of level and pitted outwash, supporting rapidly growing pure or mixed stands of jack pine and black spruce, with a blueberry–bunchberry type of ground cover.

c. *Podzolized calcareous loams and clays* (grey wooded soils) of fluvioglacial and morainic origin, supporting rapidly growing mixed stands of white spruce, balsam fir, black spruce, aspen, balsam poplar, and paper birch with ground cover of fly honeysuckle, blue bead, and club mosses.

d. *Melanized calcareous loams and clays* (boreal rendzinas) of glacial and lacustrine origin, supporting very rapidly growing stands of white spruce, balsam fir, balsam poplar, and aspen with ground association of highbush cranberry, sarsaparilla, and members of the lily family.

e. *Muck* (sapropel-like alluvial deposits) located in drainage belts and supporting non-merchantable dwarf alder and willows with a ground cover of sedges and mosses.

f. *Brown moss peat* (*Hypnum* peat), formed on fertile substrata and supporting rapidly growing stands of black spruce with some white spruce, balsam fir, aspen, and balsam poplar, and with ground cover of *Hypnum*, *Calliergon*, *Hylocomium*, and *Dicranum* mosses.

g. *Green moss peat* (*Sphagnum* peat), occupying substrata depleted in nutrients and supporting slowly growing stands of black spruce with occasional bog birch and with ground cover of *Sphagnum* mosses, leather leaf, and Labrador tea.

Morphological features of representative profiles are schematically illustrated in Fig. 1.

Further division of these broad groups could be accomplished according to classifications in current use, as exemplified by the Ontario Soil Survey reports (Hoffman, Richards, and Morwick, 1952).

Skeletal Soils

a. *Rock outcrops.* Perhaps this type of land surface illustrates better than other plant-bearing strata the modifying force of climatic factors. Since biblical days it has been an accepted idea that seed fallen on barren rock is doomed to perish. This is far from the truth in the humid environment of boreal Canada, where not only level but even nearly perpendicular outcrops of granite and schists are covered with dense stands of jack pine and black spruce. The ground cover of these sites is

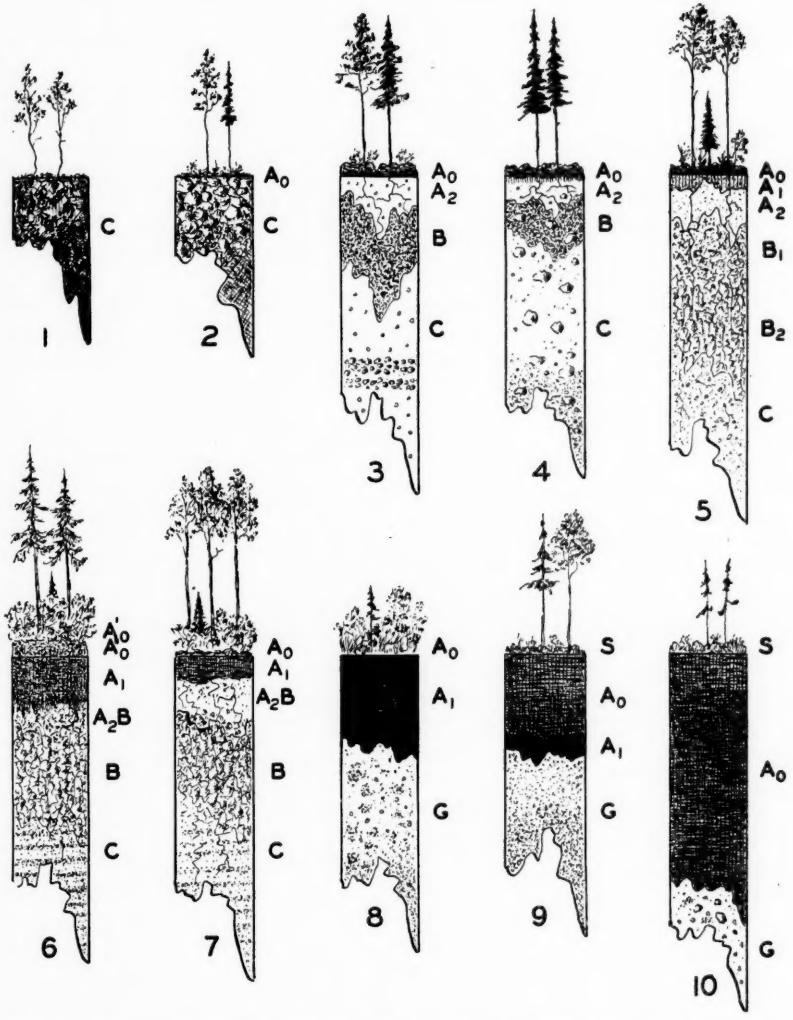

FIG. 1. Schematic presentation of typical soil profiles of the Algoma region: 1. Outcrops of crystalline rocks. 2. Granitic boulder pavement. 3. Sandy podzol on glacial outwash. 4. Sandy podzol formed on a partly assorted coarse glacial deposit. 5. Podzolized calcareous loam (grey wooded soil) developed from a loess-like material of fluvial origin. 6. Melanized calcareous varved clay (virgin phase of a boreal rendzina). 7. Melanized calcareous varved clay (burned-over phase of a boreal rendzina deprived of its thick, sawdust-like layer of 'fine mull'). 8. Muck or alder wood peat formed in alluvial channels. 9. Brown moss peat (*Hypnum* type). 10. Green moss peat (*Sphagnum* type).

formed largely by reindeer moss, *Cladonia rangiferina*, whose distribution is determined by the canopy of the forest stand (Plate 1 (*a*)). Occasionally the white blanket of the lichen is dotted by *Ledum groenlandicum* and *Vaccinium canadense* (*V. myrtilloides*).

Trees on rock outcrops depend for their existence upon the water of condensation and solid-phase feeding, and their growth is slow. Yet, in many instances, the stands attain a yield of 12 cords per acre at an approximate age of 100 years, a rate of growth comparable to that of outwash sandy soils. The utilization of these sites can be accomplished only by means of restricted selection cuttings; clear cutting is likely to place rock outcrops in the class of totally unproductive lands for many decades, if not for centuries.

b. Boulder pavements. The designation of this land type is not entirely metaphoric; in places the caprice of glaciation has produced a striking resemblance between these coarse deposits and the pre-macadam types of European highways.

On casual observation, rock outcrops and piles of boulders differ but little in their supply of water and available nutrients. Yet, boulder pavements allow deeper penetration of tree roots and accumulation of the fine mineral and organic fractions in crevices and fissures. These features, in turn, markedly increase the rate of growth of jack pine and black spruce stands which yield as much as 20 cords per acre at the age of about 70 years. An increased stability of stands and subsequent greater density of forest canopy are conspicuously reflected in the composition of ground-cover vegetation. This consists of a somewhat ragged carpet of *Hypnum* mosses and isolated specimens of *Vaccinium canadense*, *Epigaea repens*, *Ledum groenlandicum*, *Linnaea borealis*, *Maianthemum canadense*, *Cornus canadensis*, and *Lycopodium annotinum*.

Boulder pavements permit a somewhat greater freedom of cuttings than do rock outcrops, but still they must be viewed as a land type which is 'sub-marginal' for silviculture.

Sandy Podzols

This is the predominant type on coarse-textured deposits of fluvioglacial or morainic origin. The examined profiles exhibited a 2–3-inch layer of raw humus, negligible development of the A_1 horizon, and sharply delineated A_2 and B horizons. In spite of apparent profile maturity, no ortstein indurations were encountered, and the root penetration extended into the parent material. A description of a podzol profile formed under a mature stand of jack pine on a coarse outwash sand follows.

A_0: 0–2·5 in. Matted mor, consisting of a thin layer of jack pine needles and a dark brown, compressed layer of duff; penetrated by fungous mycelia and emanating a peculiar sour odour. Extremely acid.

A_1: Absent.

A_2: 2·5–9 in. Light grey, nearly white, coarse siliceous sand, with an irregular lower boundary. Strongly acid.

B: 9–21 in. Reddish to coffee-brown sand, somewhat enriched in mineral colloids and organic matter and penetrated by roots. Acid.

C: 21–45 in. Light yellow, coarse outwash sand with grit and fine gravel; extremely porous and dry at time of examination. Acid.

The results of analyses of this profile are reported in Tables 1 and 2.

TABLE 1

Reaction, Texture, Content of Organic Matter, and Exchange Properties of Upland Soils of the Algoma Region, Ontario

Horizons and their depth (in.)	*Reaction (pH)*	*Silt fraction (0·05 to 0·02 mm.) (%)*	*Clay fraction (< 0·02 mm.) (%)*	*Content of organic matter (%)*	*Exchange capacity (m.e./100 g.)*	*Total exchangeable bases (m.e./100 g.)*	*Base saturation (%)*
Siliceous sandy podzol; pioneer stand of jack pine							
A_0:0–2	4·0	..	..	89·4	59·4	21·7	36·5
A_2:2–9	4·9	4·2	1·0	1·7	6·7	1·7	25·4
B:9–21	5·6	8·0	4·8	2·5	11·8	2·9	24·6
C:21–36	5·6	1·8	0·2	0·1	0·7	0·4	57·1
Calcareous podzolized loam (grey wooded soil); pioneer stand of aspen							
A_0:0–2	6·4	..	..	80·7	79·2	65·8	83·2
A_2:2–11	5·9	65·1	8·5	1·6	15·3	9·9	64·7
B:11–30	6·5	67·0	11·0	1·2	19·3	15·1	78·3
C:30–54	8·0	80·2	6·0	0·3	22·5	39·2*	100·0
Melanized lacustrine clay (boreal rendzina); climax stand of white spruce							
A_0'':0–6	6·8	..	..	74·5	214·3	176·5	82·3
A_1:6–14	6·5	43·9	24·6	18·2	35·5	29·1	82·0
A_2B:14–35	7·0	54·3	35·4	2·6	29·8	27·6	92·6
C:35–42	7·7	37·7	55·6	0·4	25·0	49·9*	100·0

* Soil contains free carbonates.

TABLE 2

Content of Essential Nutrients and Specific Conductance of Upland Soils of the Algoma Region, Ontario

Horizons and their depth (in.)	*Total N (%)*	*Available P (p.p.m.)*	*Available K (p.p.m.)*	*Exch. Ca (m.e./100 g.)*	*Exch. Mg (m.e./100 g.)*	*Specific conductance (mhos × 10^8)*
Siliceous sandy podzol; pioneer stand of jack pine						
A_0:0–2	1·040	23	390	15·4	4·5	19·0
A_2:2–9	0·064	4	80	1·3	0·3	8·0
B:9–21	0·090	9	35	2·4	0·4	7·2
C:21–36	Tr.	2	23	0·2	0·1	2·9
Calcareous podzolized loam (grey wooded soil); pioneer stand of aspen						
A_0:0–2	1·930	49	650	51·3	9·5	31·0
A_2:2–11	0·064	6	150	5·2	1·9	9·0
B:11–30	0·062	10	142	9·0	2·4	6·2
C:30–54	0·008	4	105	30·6	6·9	11·5
Melanized lacustrine clay (boreal rendzina); climax stand of white spruce						
A_0:0–6	2·200	23	780	151·2	20·6	32·5
A_1:6–14	0·541	27	170	20·0	7·3	24·4
A_2B:14–35	0·116	65	198	19·8	3·9	15·0
C:35–42	0·050	2	242	36·9	9·5	21·3

Sandy podzols support mixed stands of jack pine and black spruce, which at times grade into nearly pure stands of either spruce or jack pine

with a spruce understorey. Occasionally there is a broadcast admixture of paper birch or an aggregate admixture of aspen. The understorey is composed of scattered balsam fir, hazelnut, and Canadian fly honeysuckle. Ground cover is characterized by the following average values for most abundant and frequent species: *Hypnum* spp. (Frequency, 100%; Coverage, 93%), *Vaccinium canadense* (Tally, 59 per 100 ft.; Frequency, 98%), *Cornus canadensis* (T, 58; F, 86%), *Linnaea borealis* (T, 38; F, 73%), *Maianthemum canadense* (T, 29; F, 76%), *Ledum groenlandicum* (T, 31; F, 57%), and *Epigaea repens* (T, 17; F, 38%). Floristically, this soil-forest unit can be appropriately designated as *Vaccinium–Cornus–Epigaea* type. It should be noted that the designation of ground-cover types was made not only on the basis of tally numbers and frequency but also with regard to a high probable occurrence and a reasonably restricted ecological amplitude.

Podzolized sandy soils are highly favourable for the growth of jack pine which often yields on these habitats 30 to 35 cords per acre at the age of about 50 years (Plate 1 (*b*)). The growth of black spruce is somewhat slower, and similar volumes are produced at the age of 70 years.

A fine-textured substratum of morainic shoulders and a ground-water table at a depth of 4 to 7 ft. are the features encouraging the development of particularly dense and heavy pine-spruce stands on podzolized sandy outwash. A similar effect is produced by thin layers of silt covering coarse glacial deposits. Such layers of aeolian or fluvial origin are quite frequent in the region studied; in spite of their thickness of only 2 or 3 in., they raise appreciably the site index of forest stands and broaden the suitability of the soil to tree species. On the other hand, a substratum of gravel or grit, encountered at a depth from 2 to 4 ft., has a tendency to lower the yields and limit the participation of spruce. In places, severe fires have reduced the average annual growth rate of jack pine to a mere quarter of a cord per acre. Stands of this kind were observed largely in the vicinity of Nipigon, a region of somewhat lower humidity.

Examination of a few stands, selectively logged by the Provincial Forest Service, suggested that the mixed jack pine-black spruce type is admirably suited for exploitation by partial cuttings. This is because of the great ecological diversity of black spruce, scarcity of competing shrubs, and very favourable conditions of moisture. Because of the market requirements, there is a pronounced feeling that silvicultural treatments should lead to a conversion of mixed stands into pure spruce forests. Such a policy would hardly be desirable, since systematic annihilation of mixed stands will definitely reduce the regional stability of forests against parasites, especially destructive insects.

Details of silvicultural management of stands on sandy podzols are well known to foresters since this type of soil received wide attention in both European and American literature (Aaltonen, 1948; Tamm, 1950; Wilde, Wilson, and White, 1949).

Calcareous Podzol Loams and Clays (*Grey Wooded Soil*)

The development of forest soils from a calcareous parent material in a humid climate is characterized by several peculiarities. Lime-bearing

deposits are enriched in essential nutrients incorporated in the remains of sea organisms (Williams, 1949). Presence of bicarbonates in the substratum leads to the accumulation of bases in the foliage, and imparts a nearly neutral or an alkaline reaction to forest litter. Under such conditions, podzolization of soil proceeds largely under the influence of biological factors, particularly fungi releasing water-soluble metabolic by-products.

In time the root systems, penetrating calcareous substrata, inflict considerable loss of calcium carbonate. This produces a change in the volume of the soil and contributes to the development of a nut structure. In soils subjected to strong percolation of water, mineral and organic compounds of calcium undergo translocation into the lower part of the soil profile, and form compacted or indurated calcareous horizons. This is accompanied by a gradual acidification of the surface soil layers. Since iron is present in limestone deposits in small amounts, its redistribution is manifested by only slightly darker shades of the accumulative horizon.

This general scheme of the metamorphism of calcareous deposits under the influence of forest vegetation is often complicated by the formation of gley layers, brought about by ground water or by seepage.

The morphology of strongly podzolized calcareous soils of the Algoma region may be exemplified by the following description of a typical profile:

A_0: 0–2·5 in. Matted mycelial mor, including litter of aspen and balsam fir and partly decomposed, compressed organic remains. This layer is penetrated by fungous mycelia and roots of ground vegetation. Nearly neutral.

A_1: 2·5–4 in. Dark grey faintly structured loam, high in organic matter and of nearly neutral reaction. In places the horizon is not discernible.

A_2: 4–11 in. Light grey loam of platy structure exhibiting pronounced signs of podzolization and with a diffuse lower boundary. Moderately acid.

B_1: 11–19 in. Transitional horizon; greyish-brown silty clay loam of faintly prismatic structure. Slightly acid; air permeability, 85 mm. Hg.

B_2: 19–30 in. Light brown, nut-structured silty clay loam with a slight greyish mottling; penetrated by coarse roots of trees. Slightly acid to neutral.

C: 30–54 in. Light brown silt loam of fluvial origin with pronounced yellowish mottling. Alkaline and high in carbonates.

Results of profile analyses are given in Tables 1 and 2.

Forest cover on podzolized calcareous loams consists of white spruce, balsam fir, black spruce, balsam poplar, trembling aspen, and paper birch. The latter two species are particularly prominent in the second-growth stands. The sporadic understorey consists of hazel, fly honeysuckle, Canadian yew, and natural reproduction of spruce and fir. The ground cover is characterized by the following data: *Clintonia borealis* (T, 18; F, 66%), *Cornus canadensis* (T, 73; F, 100%), *Maianthemum canadense* (T, 63; F, 87%), *Lycopodium* spp. (T, 56; F, 94%), *Linnaea borealis* (T, 17; F, 80%), *Aster macrophyllum* (T, 14; F, 54%), *Streptopus roseus* (T, 8; F, 37%), and infrequent *Chiogenes hispidula*, *Galium* spp., and *Ledum groenlandicum*. Floristically, this association may be classified as a *Lonicera–Clintonia–Lycopodium* type. It resembles closely the ground cover of hemlock stands on non-calcareous podzols of Canada and northern United States.

Forest stands on calcareous podzols attain high yields which sometimes exceed 40 cords per acre at the age of 70 years. This type of soil is equally well adapted to the production of pulpwood, on a short 40-year rotation, or the production of saw timber, on a rotation of 70 years. The comparative scarcity of competing shrubs and the favourable composition of the seed-bed are conducive to exploitation of mature forests by selection cuttings aiming at the regeneration of white spruce and black spruce. Clear cutting, as a rule, leads to the replacement of the climax species by less valuable pioneers—aspen and birch. Artificial reforestation of cutover areas is not justified by either economical or climatic conditions. Calcareous podzols are one form of strongly podzolized soils whose fertility level is not greatly reduced by forest fires.

Melanized Loams and Clays (*Boreal Rendzinas*)

The development of the dark A_1 horizon in some soils is attributed to the moisture conditions. Freezing of the soil surface induces the upward movement of water which saturates the surface soil below the frost line. Upon thawing, this layer remains waterlogged for a long time, which induces the accumulation of stable products of anaerobic fermentation (Williams, 1949; Gurr *et al.*, 1952).

These suggestions appear to be quite applicable to soils of the Algoma region, where deep melanized horizons are encountered predominantly in less permeable heavy soils, especially those underlain by a shallow ground-water table. A description of a typical soil profile of a melanized clay follows:

A_0':	A thin layer of litter.
A_0'': 0–6 in.	A purely organic layer of dark brown, friable sawdust-like material; ecto-humus of fine mull type. Nearly neutral.
A_1: 6–14 in.	Nearly black silt loam high in infiltrated humus, and of fine granular structure; penetrated by roots of trees and shrubs. Slightly acid.
A_2B: 14–35 in.	Transitional layer of light brown or tan silty clay loam of a platy structure suggesting initial stages of podzolization. Neutral to slightly alkaline.
C: 35–42 in.	Yellowish brown silty clay loam, exhibiting coarse, poorly defined structure, and grading into calcareous varved clay. Alkaline (pH 7·7 to 8·0).

The morphology of this profile strongly resembles that of rendzinas of Saskatchewan, as described by Putnam (1951). Tables 1 and 2 give the results of analyses of a melanized clay profile.

Although melanized clays are widely distributed in the region studied, nearly all these soils have been deprived of their original forest cover either by the axe or by fire. It is through a mere accident that the writers were fortunate to locate a few acres of this soil supporting a virgin stand. Its description follows.

The main storey is formed by white spruce with a slight intrusion of jack pine. The age of the stand varies between 90 and 150 years, and the density is about 80 per cent. of the full stocking. The average diameter exceeds 20 in. and the average height of dominant trees approaches 110 ft. The yield of standing timber was estimated between 30 and 40 m.b.f.,

or more than 100 cords per acre. The nearly impenetrable understorey, 3 to 7 ft. in height, consists of *Viburnum opulus*, *Rhamnus alnifolia*, *Acer spicatum*, *Corylus rostrata*, and *Lonicera canadensis*, with some white spruce and balsam fir saplings and seedlings. The ground cover is characterized by the following species: *Aralia nudicaulis*, *Streptopus roseus*, *Maianthemum canadense*, *Clintonia borealis*, *Trientalis americana*, *Galium* spp., *Viola pubescens*, *Aster macrophyllum*, *Fragaria virginiana*, and *Rubus villosus*.

Melanized clays under pioneer stands have the same morphology, except that the superficial layer of sawdust-like mull is greatly reduced in thickness and partly replaced by matted litter. Most of the second-growth stands are made up of balsam poplar with some aspen, white spruce, black spruce, and balsam fir. The understoreys of shrubs and ground-cover vegetation bear a close resemblance to those of the virgin stands. Balsam poplar attains at times yields exceeding 15 m.b.f., or 40 cords per acre, at the age of 70 years.

Strangely enough, under existing conditions the fast-growing stands of balsam poplar on these highly productive soils are a 'curse in disguise'; the poplar is not merchantable either as pulpwood or timber. The utilization of the enormous productive capacity of melanized clays via silvicultural crops can be achieved either through advances in wood technology or through painstaking silvicultural treatments. The latter would have to include gradual release cuttings and some artificial reforestation, either by underseeding or underplanting of white spruce. Eventually this long-time investment should bring a substantial return. Of all soils of the Algoma region, melanized clays deserve first attention as an object for intensive silvicultural management. The fact that balsam poplar is the best soil-improving hardwood of the far north is an additional consideration.

Muck Soils (*Sapropel-like Alluvial Deposits*)

The drainage belts between the elevated portions of morainic and lacustrine deposits are under the constant hydrostatic pressure of ground water deprived of its dissolved oxygen. Unless such areas have a considerable gradient or are permeated by swift undercurrents, the soil remains anaerobic. The inflow of organic colloids and soluble salts from the upland topography accumulates a rich supply of nutrients, particularly bases. The physico-chemical conditions of the drainage belts are well characterized by analysis of their ground water, presenting a natural leachate of the soil. Determinations made on water samples from these sites of the Algoma region gave the following average results: reaction, pH 6·3; redox potential, −156 mv; dissolved oxygen, 0·7 p.p.m.; specific conductance, $22{\cdot}1 \times 10^5$ mhos; total hardness, 143·7 p.p.m.

Upon the invasion of water-loving herbaceous and shrubby vegetation and the development of anaerobic organisms, the deposit gradually becomes an intimate mixture of dispersed organic and mineral particles, so-called 'muck'. This material is, in a degree, similar to 'sapropel', or a sediment formed on the bottom of lakes. The muck layer is underlain at a depth from about 1 to 4 ft. by a mottled gley horizon of nearly

neutral or alkaline reaction. The average state of fertility factors in a representative profile of muck soils is given in Table 3.

TABLE 3

Chemical Properties of Representative Profiles of Organic Soils of the Algoma Region, Ontario

Horizons and their depth (in.)	Reaction (pH)	Spec. cond. (mhos × 10^4)	Organic matter %	Total N %	C/N ratio	Exch. capacity (m.e./100 g.)	Exch. Ca (m.e./100 g.)	Exch. Mg (m.e./100 g.)	Avail. P (p.p.m.)	Avail. K (p.p.m.)
Muck (finely dispersed wood peat); hoary alder										
A_0': 0–6	5·4	38	82·6	2·06	23·0	114·3	73·2	19·7	55	775
A_0'': 6–27	5·3	17	79·7	1·93	25·1	101·6	65·0	14·5	38	565
G: 27–36	7·2	27	1·2	0·02	..	22·7	72·0*	7·7	12	265
Brown peat (*Hypnum* type); black spruce with some white spruce and balsam poplar										
A_0': 0–6	5·7	30	90·0	1·20	40·5	87·9	48·9	12·9	77	595
A_0'': 6–23	5·3	22	85·4	1·29	36·2	123·7	81·5	17·4	28	455
G: 23–30	7·6	23	0·6	0·01	..	18·6	95·7*	3·3	12	175
Green peat (*Sphagnum* type); black spruce with some bog birch										
A_0': 0–6	4·3	23	92·0	1·08	46·0	70·8	38·5	6·2	42	330
A_0'': 6–24	4·7	18	92·9	1·30	35·8	92·3	45·6	8·5	43	415
A_0''': 24–36	5·4	25	88·0	1·37	36·6	79·5	47·0	9·2	24	335
G: 42–50	6·8	29	9·2	Tr.	..	21·1	17·4	3·8	3	155

* Contains free carbonates.

The enrichment of muck soils in nutrients induces the development of extremely dense, jungle-like stands of hoary alder, or other species that can tolerate stagnation and withstand competition of alder.

The composition of vegetative cover on muck soils studied is given by the following average data: alder (C, 62·5%), willow spp. (F, 27%), trembling aspen (F, 10%), balsam poplar (F, 5%), balsam fir (F, 29%), black spruce (F, 18%), white spruce (F, 10%), and dogwood (F, 23%). The dominant mass of ground vegetation is formed by *Carex* spp (F, 70%; C, 27%), and mosses, particularly those of *Sphagnum* genera, *Calliergon Schreberi*, and species of the *Hypnum* group. Among the characteristic lesser vegetation, *Aralia nudicaulis* (T, 5; F, 34%), *Coptis trifolia* (T, 16; F, 53%), and *Rubus villosus* (T, 40; F, 52%) stand out. Other members of the ground cover are *Viola pubescens* (T, 25; F, 57%), *Galium triflorum* (T, 6; F, 17%), *Vaccinium canadense* (T, 4; F, 14%), and *Ribes lacustra* (T, 2; F, 13%). Occasionally the association is enriched with invaders from adjacent moss-peat swamps, namely, *Ledum groenlandicum*, *Vaccinium oxycoccos*, *Chamaedaphne calyculata*, *Kalmia polyfolia*, and especially *Andromeda glaucophylla*.

Forest cover on this soil type produces at best only a few cords of pulpwood, and commercially is a liability rather than an asset. This is especially true because alder tends to spread to the neighbouring cut-over lands of high productive potential and thus to interfere with the natural

regeneration of spruce. Yet belts of dense alder brush, forming a network over the entire Algoma region, have a great value from the standpoint of forest protection. Alder is one of the most fire-resistant species of the plant kingdom, and it provides natural fire-breaks. To some degree these isolation strips check the spread of parasitic insects. Moreover, alder is a nitrogen-fixing species, and has a base-enriched litter; it intercepts and transpires enormous quantities of water. It plays a concealed but extremely important part in the maintenance of the productive capacity of cut-over and burnt-over soils of the north. All in all, if elimination of alder were threatened by deadly parasitic organisms, in time forest management would probably seek methods for the preservation of this now rejected and despised member of the forest community.

Brown Moss Peat (*Hypnum Peat*)

This type may be regarded as an early stage of successional development of organic soils which proceeds today in the entire sub-tundra zone of the northern hemisphere. This trend is indicated by the works of Finnish foresters and soil specialists, who come in daily contact with the menace of 'swamp encroachment', and who should be considered as the foremost students of the boreal deposits of peat.

In the Algoma region, brown moss peat is confined to the potentially fertile, lime-enriched substrata, and in terms of Finnish classifications belongs to the 'Korpi' group, or more specifically to the 'Lettokorpi' type. The latter *via* 'Lettoräme' eventually culminates in the 'Neva' group (Huikari, 1952).

The entire process of peat metamorphism resembles the course of a river. Brown moss peat springs up in the form of a raw humus or a 'bog mor' on any exposed fertile substratum that is capable of accumulating vadose water. In time the layer of dead *Hypnum* mosses increases in thickness, as well as in acidity and the content of reducing substances. At a certain point the fixation of available nutrients by moss tissues opens channels for the inflow of *Sphagnum* species. These gradually transform the deposit into the yellowish-green 'Neva', a treeless swamp dominated by sedges or *Sphagnum fuscum*.

The present studies indicate that these dynamics of peat soils cannot always be arrested even by the high content of carbonates present in clays of lacustrine origin. On substrata poor in bases, the brown-moss stage is likely to be of short duration, or it may be entirely eliminated by the direct invasion of *Sphagna* and low acidophilous shrubs. In several instances the invasion of many *Sphagnum* species was recorded on soils of nearly neutral and alkaline reaction (pH 6·7 to 7·3), disproving the prevailing contention that the distribution of these plants is confined to acid soils. Once established, however, *Sphagnum* does have a tendency to acidify the invaded substratum.

The depth of the Algoma brown moss peat varies between 8 in. and about 3 ft. The shallow variety is formed by a layer of a saprogenous moss mor, resting either on podzolized calcareous soils or on lacustrine rendzinas with well-developed melanized layers. The arbitrary thickness of the organic layer, exceeding 8 in., is the only criterion which

differentiates youthful brown moss peat from gley soils. The deep varieties usually contain remains of *Sphagna* in their surface layers and cannot be readily separated from green moss peat. The following profile description typifies a transitional variety of brown moss peat in the pre-sphagnum stage of development.

A_0: 0–18 in. Brown to dark brown matted remains of mosses, largely of *Hypnum* genera, and other ground-cover plants; the layer includes some fragments of wood and is penetrated by a network of dead and living tree roots. Moderately acid.

A_1: 18–23 in. Dark brown, nearly black mixture of finely dispersed organic matter and clay. Acid.

G: 23 in.+ Mottled calcareous clay of strongly alkaline reaction. Ground water of a very low temperature (3° C.) was encountered at the depth of 37 in.

Results of analyses of a representative brown moss peat profile are given in Table 3.

The forest cover on brown moss peat is made up of black spruce, white spruce, and balsam fir, with occasional occurrences of balsam poplar and aspen. The ground cover is formed by a continuous 'stratum superficiale' (Forsslund, 1943) of *Calliergon Schreberi*, *Hypnum crista-castrensis* and other *Hypnum* spp. with a sporadic occurrence of *Hylocomium splendens*, *Dicranum rugosum*, *Paludella*, *Helodium*, *Scorpidium*, *Drepanocladus*, and some *Sphagnum* spp., particularly *S. acutifolium* and *S. squarrosum*. The herbaceous and low-shrub vegetation is characterized by the following average data: *Ledum groenlandicum* (T, 45; F, 98%), *Cornus canadensis* (T, 37; F, 100%), *Vaccinium canadense* (T, 14; F, 87%), *Maianthemum canadense* (T, 16; F, 77%), *Rubus villosus* (T, 16; F, 62%), *Aster macrophyllum* (T, 11; F, 62%), *Viola pubescens* (T, 6; F, 32%), *Galium triflorum* (T, 5; F, 23%), *Trientalis americana* (T, 3; F, 12%), *Coptis trifolia* (T, 8; F, 18%), *Vaccinium oxycoccos* (T, 3; F, 23%), *Linnaea borealis* (T, 4; F, 17%), and *Ribes lacustra* (T, 2; F, 12%).

Forest stands on this type of soil attain high yields of 30 cords per acre at the age of 70 to 90 years. The rate of growth is even higher on shallow peat, but drops off to about one-quarter of a cord per acre per year on deep peat invaded by *Sphagnum* species.

The development of peat soils on upland topography leaves no doubt that under existing climatic conditions the removal of forest cover, or even a considerable opening of the canopy, will increase soil moisture in the surface layers and will accelerate the invasion of Sphagnaceae. This, in turn, means increased anaerobiosis, irreversible fixation of nutrients, and adverse insulating effect of bog moss. The latter amplifies the discrepancy between the temperatures above and below the ground line. Therefore the preservation of the high productive capacity of brown moss peat can be achieved only through very conservative partial cuttings.

The present, universally adopted system of clear cutting swamp forests is harmful in two different ways: it deteriorates the inherent quality of sites, and it eliminates from the production cycle the timber stock of high growth potential. The ill effects of the swamping process are not as conspicuous as those of forest fires, but they are more dire in consequence;

they may persist for centuries. Brown moss peat is an extremely important asset of the pulp and paper industry of North America, and the conversion of these productive organic soils into *Sphagnum* muskegs will inflict enormous losses on the Canadian government and private land owners.

Fortunately, in some instances, the deterioration of fertile peat deposits due to clear cutting is retarded by a rapid invasion of alder. This act of nature interferes with the immediate regeneration of spruce, but it preserves the productive capacity of the soil for future generations of trees.

Green Moss Peat (*Sphagnum Peat*)

Green moss or *Sphagnum* peat is the predominant type of soil in the region studied. It is particularly common on extensive flat areas of different elevations and in depressions of morainic deposits (Plate I (*c*)). Occasionally it is found on tops of hills and ridges underlain by strata of low permeability.

Generally the development of this type is promoted by the stagnant condition of ground water and by the initial poverty of parent material. In many instances, however, encroachment of *Sphagnum* is a result of fire or wind destruction of upland forest and subsequent accumulation of vadose water in the surface layers of soils. Otherwise, green moss swamps present a successional stage superseding the brown moss swamps.

Thus the collective expression 'green moss peat' refers to a whole series of types determined by the position of the ground-water table, the rate of subterranean drainage, fertility level of the substratum, and stage of succession. One extreme of this series is characterized by a shallow depth, moderate acidity, and a fair rate of forest growth. The other extreme is characterized by a considerable depth, strong acidity, and a very low rate of forest growth. The average conditions of the soils and forest growth are presented by the transitional varieties, as exemplified by the following description:

A_0: 0–36 in. Slightly decomposed remains of *Sphagnum* mosses of yellowish green colour and fibrous structure. The layer is penetrated by living and dead roots and contains some fragments of wood. The lower portion of the horizon is of a brownish colour and is enriched with the remains of cotton grass, sedges, and other vegetation. Strongly acid.

A_1G: 36–42 in. A transitional layer of grey clay infiltrated with organic colloids. Moderately acid.

G: 42 in.+ Light grey mottled clay. Slightly acid.

Results of analyses of a representative peat profile are reported in Table 3.

Green moss peat in the Algoma region, as a rule, supports only one tree species, black spruce (Plate I). There are occasional trees of bog birch, alder, and willow. The ground cover of reasonably productive sites has the following features: *Sphagnum* spp. (F, 100%; C, 97·5%), *Chamaedaphne calyculata* (T, 72; F, 100%), *Kalmia polyfolia* (T, 32; F, 84%), *Andromeda glaucophylla* (T, 23; F, 67%), *Vaccinium canadense* (T, 10; F, 42%), *Ledum groenlandicum* (T, 17; F, 65%), *Vaccinium*

oxycoccos (T, 7; F, 23%), *Betula pumila* (T, 23; F, 67%), *Salix pedicullaris* and related species (T, 7; F, 14%), with incidental occurrence of *Carex* spp., *Eriophorum* spp., *Rubus chamaemorus*, *Menyanthes trifolia*, and *Sarracenia purpurea*. The younger and usually shallower swamps of this type are characterized by the presence of *Sphagnum acutifolium*, *S. squarrosum*, and *S. compactum*. The older and deeper swamps have a predominance of *S. amblyphyllum*, *S. subsecundum*, *S. papillosum*, *S. recurvum*, and especially *S. fuscum*.

The productive capacity of green moss peat varies within the very broad range of 3 and 15 cords per acre at the age of about 100 years. A wide variation in yields of timber is often observed at practically the same site index because of the differences in the degree of stocking. The entire crop finds only one outlet, as pulpwood.

From an abstract point of view, silvicultural management of this soil-forest type should follow the principles outlined for the brown moss peat. However, it is clear that in the present economic milieu, the slowly growing stands of black spruce cannot justify the cost of intensive silvicultural management. Therefore the only requirement which a practising forester should bear in mind is the restriction of clear cutting to possibly small, dispersed areas. This is essential because extensive cut-over lands create serious danger of forest fire; they provide readily combustible material and give the wind an opportunity to attain great velocity. In the inaccessible environment of the Algoma region, forest fire is the greatest enemy of the forestry enterprise.

TABLE 4

Analysis of Ground Water in Black Spruce Stands of the Newaygo Timber Co., Ltd., Vicinity of Hearst, Ontario, Canada. (Yields in Standard Cords at an Approximate Age of 100 Years)

Type of peat, composition, and rate of growth of forest stand, and nature of ground cover vegetation	*Min. and max. values determined*				
	Reaction (pH)	*Redox potential (m.v.)*	*Dissolved oxygen (p.p.m.)*	*Specific conductance (mhos × 10^5)*	*Hardness as $CaCO_3$ (p.p.m.)*
Deep green moss peat. Unproductive *Sphagnum* with cotton grass, sedges, and low shrubs.	5·5 6·1	−222 −147	Tr. 1·4	3·8 5·4	2·4 34·0
Green moss peat. Black spruce with some bog birch; slow growth —5 to 10 cds/A. *Sphagnum*, *Ledum*, *Kalmia*, *Andromeda*, and *Rubus chamaemorus*.	5·9 6·5	−163 −127	Tr. 2·3	5·7 12·2	32·5 90·1
Brown moss peat. Black spruce with some balsam fir; fair growth —15 cds/A. *Calliergon Schreberi*, brown mosses, *Vaccinium*, and *Cornus canadensis*.	5·7 6·7	−170 −121	0·9 2·6	3·2 18·0	27·7 115·2
Shallow brown moss peat (transition to gley soils). Black spruce with some balsam fir and balsam poplar; rapid growth—25 to 35 cds/A. *Hypnum*, *Calliergon*, *Dicranum*, *Cornus*, and *Lycopodium* spp.	6·7 7·2	−131 −103	2·0 4·1	14·4 28·7	77·8 185·0

Clear cuttings on this particular type of peat enjoy one definite advantage: natural reproduction of spruce is only slightly handicapped in its development by alder and other competing vegetation. The process of natural regeneration usually may be enhanced by making provision for the source of seeds. This can be best accomplished by leaving undisturbed groups of trees, large enough to resist the force of wind. Leaving suppressed and otherwise inferior seed trees violates the principles of genetics and threatens to bring about a progressive degeneration of growing stock.

Table 4 presents the analytical data indicating the general trend in the chemical composition of ground water underlying different types of green moss and brown moss peat of the Algoma region.

Acknowledgements

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Forest types of the Algoma region, northern Ontario. a. Pioneer stand of jack pine with a snow-white ground cover of *Cladonia rangiferina* on granitic outcrops; b. Rapidly growing stand of jack pine with some black spruce and with a ground cover of *Vaccinium-Cornus* type on a coarse-textured podzol; the volume of timber is indicated by the cord wood removed from the road strip; c. Slowly growing stands of black spruce of *Ledum-Chamaedaphne* type on Sphagnum moss peat.

S. A. WILDE, G. K. VOIGT, R. S. PIERCE—PLATE I

A STUDY OF PODZOLIZATION

III. THE MOBILIZATION OF IRON AND ALUMINIUM BY RIMU (*DACRYDIUM CUPRESSINUM*)

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In previous communications (Bloomfield, 1953) an account has been given of the podzolizing properties of Scots pine and kauri debris. It was shown that aqueous extracts of the litter of these trees were capable of causing solution and reduction of ferric oxide under conditions at once aerobic and alkaline. The extension of this investigation to cover Norway spruce, Sitka spruce, Douglas fir, and the rimu of New Zealand (*Dacrydium cupressinum*) has shown that to a greater or less extent these properties are shared by all the species studied. Of these species the rimu, in addition to being the most active in mobilizing iron, showed certain peculiarities which appear to merit its individual consideration.

The rimu grows in most parts of New Zealand, and its timber is extensively exploited for building and furniture making. Like the kauri, the rimu sheds its bark in large flakes, but these do not accumulate to the same extent as does the bark of the kauri.

Experimental

Rimu foliage consists of long slender fronds bearing small and closely spaced spike-shaped leaves. Because of the difficulty of removing the leaves from the stem, and as the whole frond is cast off by the tree, no attempt was made to deal with the leaves separately. The fronds were dried at 50–60° C. and ground in a Raymond mill. The bark was broken into small pieces and ground similarly, without previous drying.

Aqueous extracts of the leaves and bark were prepared by shaking the ground materials with water for about 12 hours and filtering. As with kauri, the rimu bark gave a very intensely coloured solution.

Solution of ferric and aluminium oxides

The non-biological solution of ferric and aluminium oxides by 5 per cent. extracts of the leaves and bark was investigated in the manner previously described (Bloomfield, 1953). As before, the process was examined under aerobic and anaerobic conditions at high and low pH values, the latter being the pH of the untreated water extracts.

The results are illustrated in Fig. 1, from which it can be seen that, as in the case of kauri, the leaves are very much more effective in mobilizing the sesquioxides than is the bark. (Since it showed such slight activity, only one curve for the bark extract is given in the figure.) All the solutions gave positive reactions for ferrous iron with dipyridyl, but sorption of ferous dipyridyl on organic matter, which was coagulated on addition of electrolytes, prevented estimation of the ferrous content.

It can be seen from Fig. 1 that at pH 4·1 and under aerobic conditions the rimu leaf extract shows an important difference from the species

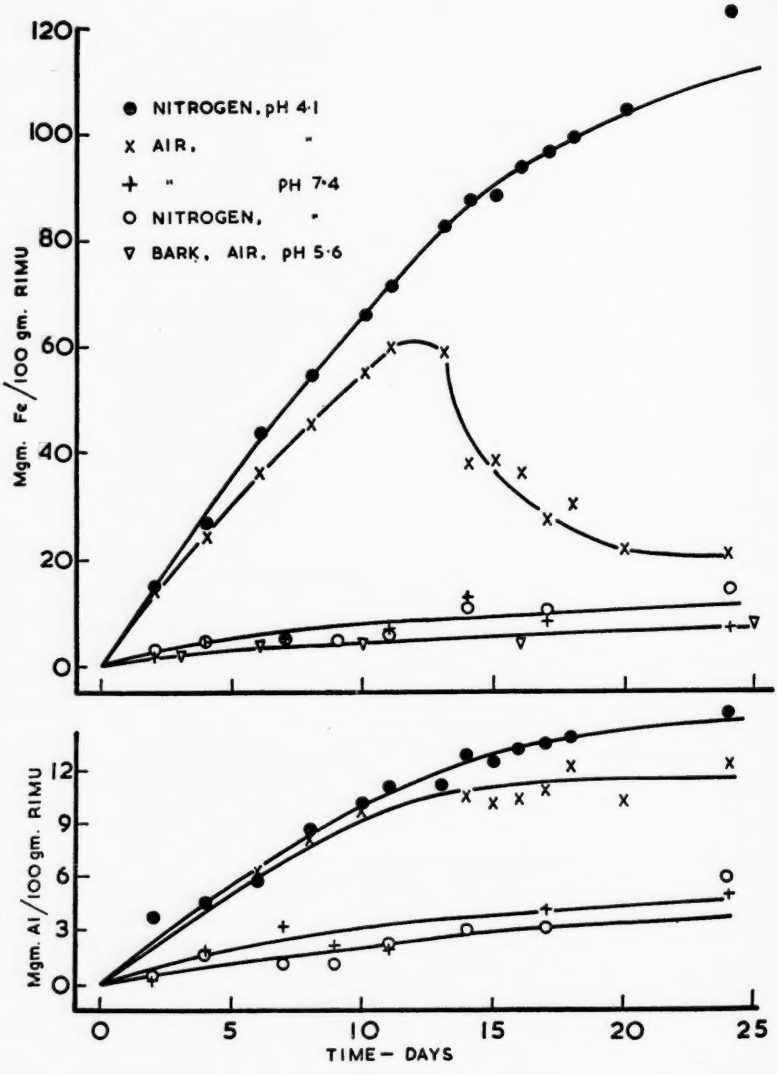

FIG. 1.

previously reported, in that the concentration of dissolved iron falls off rapidly after about 12 days. As no such decrease takes place in the absence of oxygen, a possible explanation is that oxidation and conse-

quent precipitation of ferric oxide is the cause of the decrease in concentration, but the abrupt change is difficult to reconcile with this view, since the reaction mixture was maintained under fully aerobic conditions throughout the whole period.

A marked feature of the reaction was the pronounced colour change undergone by the reaction mixture. In all cases the solution, originally light brown in colour, became very dark after a few days while the undissolved sesquioxides become quite black. In the case of the aerobic reaction at pH 4·1, the decrease in the concentration of dissolved iron

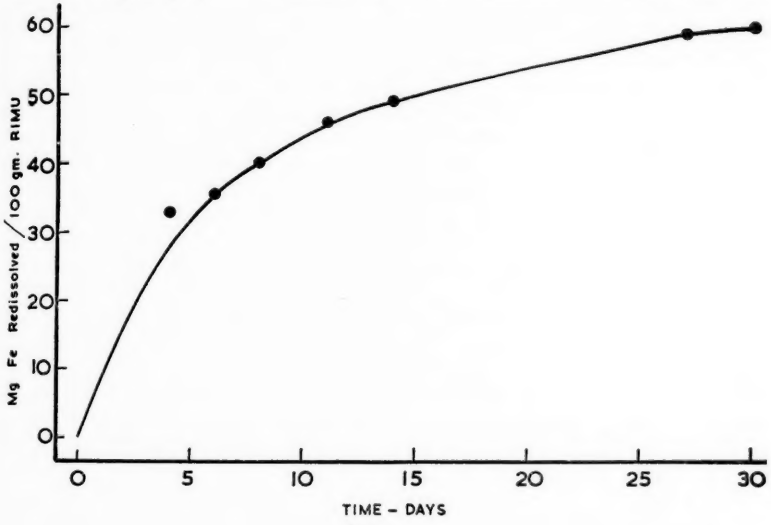

FIG. 2.

was accompanied by the formation of a flocculent precipitate, at first black in colour, later changing to dark brown; at the same time the solution lost its intense colour, eventually becoming pale brown.

In order to determine whether this precipitate consisted of an iron compound capable of resisting the solvent action of the rimu leaf extract, a portion of the precipitated material was washed with water to remove soluble ferrous compounds, particles of the original ferric oxide being removed at the same time by sedimentation—the flocculent nature of the precipitate made this a relatively easy matter. The washed precipitate was then treated with a fresh leaf extract, again under aerobic conditions. Periodic determination of the dissolved iron gave the results illustrated in Fig. 2, from which it can be seen that although solution of the iron proceeded readily, no tendency for the iron to precipitate was exhibited over a period of some 30 days, in contrast to the original experiment in which the precipitation was completed in about 15 days.

The precipitate used as the starting material in this experiment contained an appreciable amount of organic matter; solution of the precipitate would therefore result in a solution of higher organic/iron ratio than

that produced in the preceding experiment. It is possible that the relatively greater concentration of organic compounds in the reaction solution was responsible for the retention of the iron in solution. If this supposition is correct, there should exist an organic/iron ratio above which no precipitation will occur when the solution undergoes atmospheric oxidation. However, there are indications that other factors may also be involved.

Reoxidation of the ferrous-rimu complex

The behaviour of the ferrous-rimu compound on oxidation is of obvious interest in connexion with the precipitation phenomenon discussed in the previous section. The rate of oxidation of the ferrous compound was determined by aerating a solution which had been obtained by anaerobic treatment of ferric oxide with a 5 per cent. rimu extract for 30 days. The experiment was carried out at pH values of 3·8 and 7·0 as described in the earlier papers of this series. The reaction between dipyridyl and the ferrous iron in the reaction solution takes some 24 hours to reach equilibrium, indicating the complex nature of the ferrous-rimu compound. In this experiment, however, development of the ferrous dipyridyl colour on standing was accompanied by the formation of a precipitate on which the dipyridyl complex was sorbed to some extent. It was only possible, therefore, to determine the variation in the total iron content as the solution oxidized. The results, given in Fig. 3, show that at pH 3·8 the ferrous-rimu compound is readily oxidized until, for a 5 per cent. leaf extract, the concentration falls to about 15 mg. iron per litre, at which concentration the iron appears to be indefinitely stable with respect to precipitation, if not to oxidation. Raising the pH to 7·0 precipitates all but approximately the same amount of the iron; probably the same stable fraction is involved in each case. At the end of the experiment, i.e. after 24 days' aeration, the residual solutions still gave positive reactions for ferrous iron with dipyridyl.

It has been found that although this experiment can be repeated to obtain the same qualitative results, quantitatively the agreement is not very close. A comparison of the various sets of results which have been obtained suggests that here again the factor determining the course of the reoxidation may be the organic/iron ratio of the ferrous-rimu solution, but this point requires further experimental study.

Different methods were used in preparing the rimu- and kauri-ferrous solutions for the oxidation experiments, and no doubt this is largely responsible for the observed differences between the two species. In preparing these solutions, one is faced with a dilemma since solution of ferric oxide by the leaf extracts is relatively slow, and, for any reasonable time of reaction, results in a solution which still possesses a considerable capacity to reduce ferric iron; the objections to using such a solution for oxidation experiments are obvious. On the other hand, addition of a ferric salt to a leaf extract, the method used with the kauri, while free from the previous objection, is unsatisfactory owing to the unavoidable introduction of extraneous anions. With the exception of Scots pine,

addition of ferric salts to the extracts causes separation of bulky precipitates, and it is difficult to predict what would be the effect of the removal of this relatively large fraction of the organic matter. In the case of the

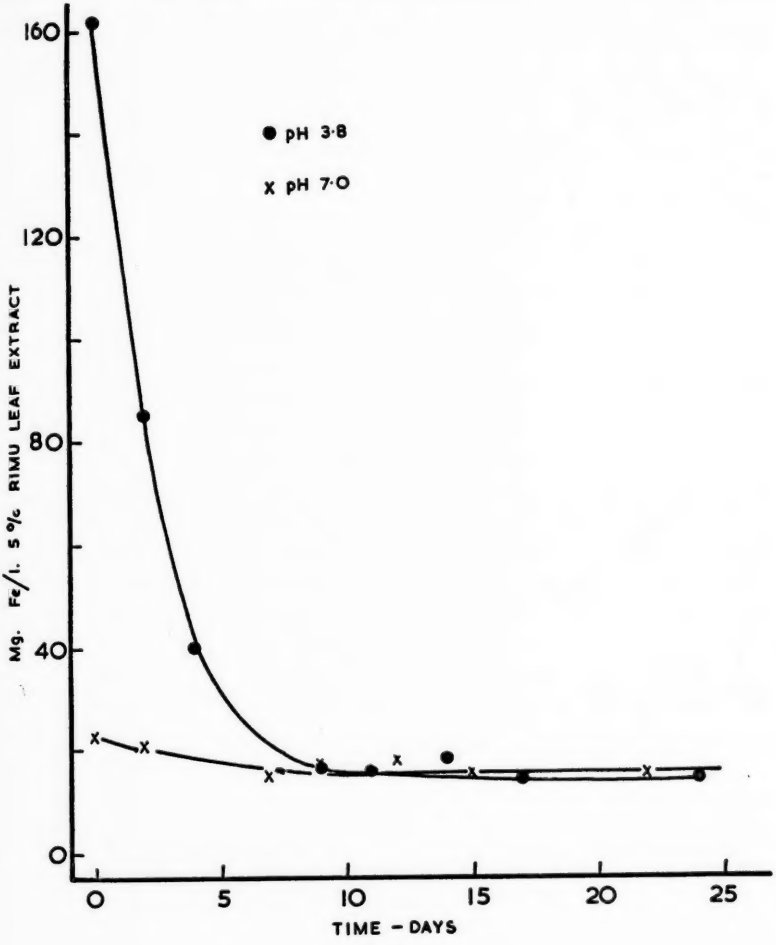

FIG. 3.

rimu extract, addition of ferric salts caused the formation of a very bulky precipitate, and was accompanied by such marked colour changes that it was thought advisable to adopt the alternative method. It may be noted that if a kauri-ferrous solution is prepared by treatment of ferric oxide with the leaf extract, the behaviour of the resulting compound when oxidized is comparable with that of the rimu system, although here again the quantitative reproducibility of the reaction is not of a very high

order. For this reason there is little point in attempting a precise comparison of the oxidation characteristics of the two species until more is known about the variables which control the two systems.

Variation of the solubilities of iron and aluminium with pH

In this experiment the iron and aluminium solutions were prepared as were those used in the previous experiment, i.e. by treatment of the hydrous oxide with an aqueous leaf extract. Except for the difference in the method of preparation of the solutions, the determinations were carried out as described previously, calcium hydroxide being used to adjust the pH. The results are given below.

	mg./l. retained in solution 10% leaf extract	
pH	*Fe*	*Al*
3·8	73·6	..
6·0	73·4	..
8·0	9·0	..
4·1	..	47·6
6·0	..	36·2
8·0	..	4·6

Because of the method of preparation, the original solutions were not saturated with their respective cations, and consequently the concentrations obtained at the two higher pH values can only be regarded as saturation concentrations if they are significantly lower than the preceding value. Thus the figures quoted for iron at pH 3·8 and 6·0 must be regarded as lower than the theoretical values.

It appears from the results that both the iron and aluminium were present in complex forms which are decomposed at pH 8.

Discussion

Comparison of the results obtained for the solution of the hydrous sesquioxides by rimu and kauri leaves shows that the former is rather more active than the latter: in the relatively low activity of their bark extracts, the two species behave similarly.

It is a matter of field observation that while the kauri is a very active podzolizing agent, the rimu is considerably less so; clearly then, factors additional to those considered here must operate under natural conditions. In the first place, the nature of the soil must play an important part in determining the rate of podzolization by any given species, since the ease of solution of both ferric and aluminium oxide may vary between wide limits, depending on the previous history of the material. However, the field evidence does not suggest that variations in the parent material could be the cause of this particular discrepancy. It must not be overlooked, however, that a valid comparison of the two species on the basis of the laboratory investigation is not possible without a knowledge of the weight of litter produced annually in each case; it may well be that the

difficulty in reconciling the laboratory and field observation results from the use of the weight of dry leaves as the basis for comparison.

Although the rimu-ferrous complex is less stable at high pH values than those of Scots pine and kauri, nevertheless it is sufficiently stable to indicate that precipitation of the oxide cannot be caused by the relatively small changes in pH that are likely to occur in the soil. The relative ease with which the rimu complex is oxidized, however, suggests that this factor may well play an important part in the formation of the B_2 (iron) horizon. No such explanation can be postulated to account for the precipitation of the aluminium to form a separate horizon, and it seems probable that the first stage in the immobilization of the sesquioxides is a sorption of the complexes on the soil material, in particular on sesquioxides; the separation of the iron and aluminium in successive horizons could then be explained by analogy with a chromatographic column; reoxidation of the sorbed ferrous compounds would presumably take place whenever there is free access of air. If the results obtained in experiments on the sorption of ferrous ions on ferric oxide (Bloomfield, 1951) are also true for the complexes involved here, the oxidation of the ferrous complex in the sorbed state should take place more readily than when in solution.

Summary

The action of aqueous extracts of rimu litter on hydrous ferric and aluminium oxides closely resembles that of Scots pine and kauri. The oxides are dissolved with the formation of organic complexes, the ferric iron suffering reduction even in the presence of atmospheric oxygen.

Acknowledgements

The author wishes to thank Messrs. N. K. Taylor and C. F. Sutherland, and Major A. A. Dorrien Smith who provided the rimu material used in this study.

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A STUDY OF PODZOLIZATION

IV. THE MOBILIZATION OF IRON AND ALUMINIUM BY PICKED AND FALLEN LARCH NEEDLES

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THE previous papers of this series have given the results of experiments on the mobilization of soil sesquioxides by water extracts of the foliage of certain species of conifers (Bloomfield, 1953, 1954). Because of the non-deciduous nature of these conifers, it was not possible to obtain adequate samples of freshly fallen litter, and consequently the work was carried out using needles picked from the tree. As it was not known to what extent the properties of the foliage change before it falls from the tree, it remained uncertain how far the results obtained in the laboratory could be claimed to apply to a forest soil in which the dynamic of sesquioxide translocation is provided, at least in part, by the constituents leached from the fallen material. It was therefore of obvious interest to compare the properties of picked and fallen larch needles, the deciduous nature of the larch making it possible to obtain the latter in reasonable quantities.

Experimental

The picked needles were collected in the early autumn, before they had begun to turn yellow. The fallen needles were collected on tarpaulins and gathered at frequent intervals to avoid leaching by rain. In both cases the needles were dried at 50° C. and ground to a fine powder.

The properties of water extracts of the two samples were compared using the same experimental methods as described previously.

Effect of pH and aeration on the solution of ferric and aluminium oxides

The pH of a 5 per cent. water extract of both the picked and fallen needles was 4·5. Experiments were carried out at this pH and also at pH 7·0, sodium hydroxide being used to obtain the latter value.

It was found that the two extracts did not differ significantly in their ability to dissolve aluminium oxide; the curves relating to the picked needles have not, therefore, been included in Fig. 1.

It can be seen from the figure that at the lower pH the needles differ in their iron-mobilizing properties, and that, contrary to expectation, the fallen needles are the more active. More surprising is the greater activity of the fallen needle extract in the presence of air.

It has been observed previously that for a number of species the activity of picked needles decreases appreciably on being dried, so that it is possible that the greater activity of the fallen needles may be due to the fact that the picked needles required an appreciably longer period at 50° C. before they were sufficiently dry to be ground. No undried fallen needles were available at the time when this difficulty was appreciated.

At pH 7 the larch extracts retained very little of their dissolving properties.

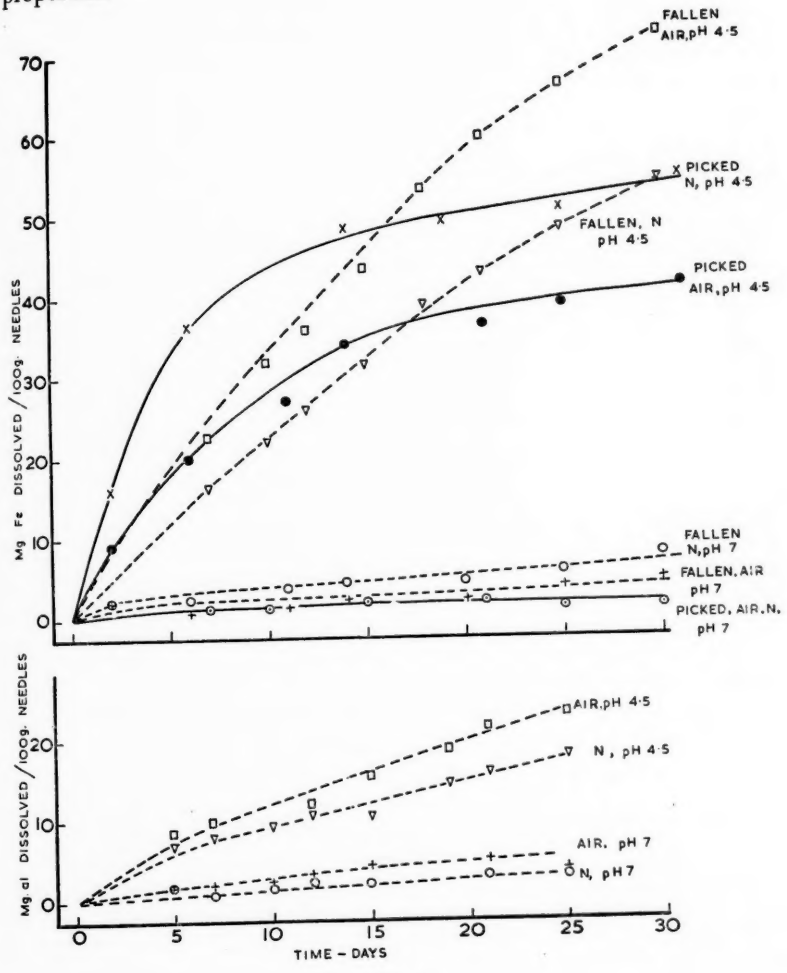
FALLEN AIR, pH 4·5
PICKED N, pH 4·5
FALLEN, N pH 4·5
PICKED AIR, pH 4·5
FALLEN N, pH 7
FALLEN, AIR pH 7
PICKED, AIR, N. pH 7
Mg Fe DISSOLVED / 100g. NEEDLES
AIR, pH 4·5
N, pH 4·5
AIR, pH 7
N, pH 7
Mg al DISSOLVED / 100g. NEEDLES
TIME - DAYS

FIG. 1.

Reoxidation of ferrous larch solutions

The ferrous solutions used in these experiments were prepared by the anaerobic treatment of ferric oxide with 5 per cent. extracts of the needles. Oxidation was effected by shaking the solutions in partly filled reagent bottles. As with the rimu solution, the presence of coagulatable organic matter made determination of the residual ferrous iron impossible; consequently only the total iron remaining in solution was

measured. This, of course, is a function of the overall oxidation-precipitation process.

The results are illustrated in Fig. 2. The relation between the two ferrous solutions is what would be expected from the results of the preceding experiment, in that the picked needle preparation is the most readily oxidized.

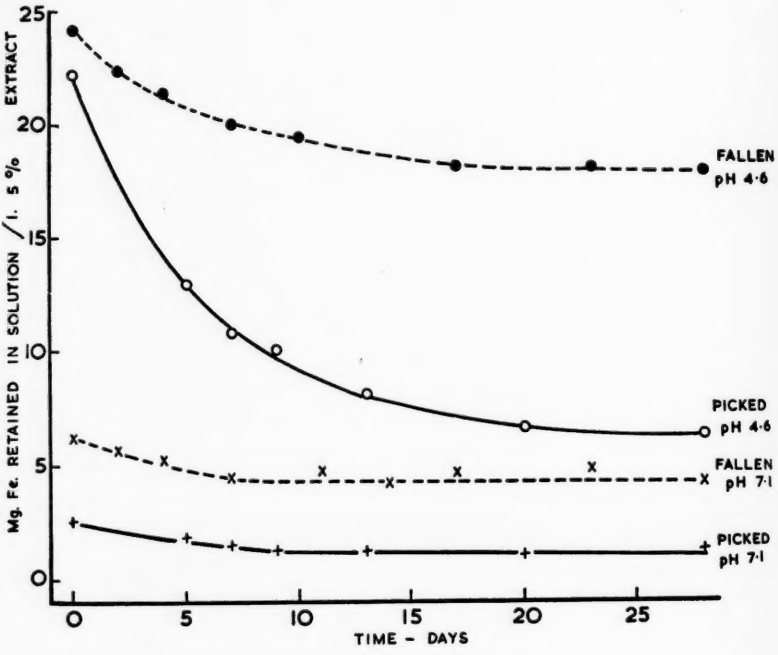

FIG. 2.

Variation of the solubilities of iron and aluminium with pH

Iron and aluminium solutions, prepared by treatment of the respective oxides with 10 per cent. aqueous extracts of the needles, were treated with calcium hydroxide to give predetermined pH values and centrifuged. The concentrations of iron or aluminium remaining in solution were then determined in the usual way.

The results are given below; it is seen that once more the fallen needles exert the greater effect.

Discussion

The results obtained in these experiments show that in its action on ferric and aluminium oxides, aqueous extracts of autumn fallen larch needles behave in the same qualitative manner as extracts of the picked needles; furthermore, the action of the larch extracts differs only in degree from that of the coniferous species previously studied. Since the

Fallen needles			*Picked needles*		
	mg./l. retained in solution 10% extract			*mg./l. retained in solution 10% extract*	
pH	*Fe*	*Al*	*pH*	*Fe*	*Al*
4·6	68·0	..	4·5	49·6	..
6·0	63·8	..	6·0	40·4	..
8·0	38·0	..	8·0	29·4	..
4·8	..	30·6	4·6	..	28·2
6·0	..	19·6	6·0	..	17·8
8·0	..	16·4	8·0	..	12·8

difference between picked and fallen larch needles is in this respect so small it is justifiable to assume that the results obtained with the picked needles of other conifers are equally applicable to the fallen needles of the same species, and hence to the soil processes.

In a recent note Schnitzer and DeLong (1952) stated that naturally formed leachates of various types of forest litter show the same general properties as those described in this and the previous papers of this series; it must therefore be conceded that the reactions described here take place, at least to some extent, in the soil.

In view of the relative stability of the ferrous solutions to oxidation, it seems that in a soil, where conditions would not be expected to be at all strongly oxidizing, translocation of the iron would take place with the iron in the form of a ferrous complex.

Summary

The water extracts of larch needles exhibited the same ability to dissolve ferric and aluminium hydrous oxides as was observed with non-deciduous conifers. Only quantitative differences existed between picked and fallen needles.

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A STUDY OF PODZOLIZATION

V. THE MOBILIZATION OF IRON AND ALUMINIUM BY ASPEN AND ASH LEAVES

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PREVIOUS papers in this series (Bloomfield, 1953) have dealt with the mobilization of hydrous sesquioxides by various coniferous species. Although podzolization is generally associated with a coniferous or heath cover, cases are known in which leaching of sesquioxides occurs under broadleaved species. The earliest description of the very strong bleaching that can take place in such cases is probably that of Popov (1914), who described the development of the soils of the aspen groves of the Voronezh region of central Russia. These soils appear to belong to the solonetzous and solod types, but in these groves 'the solonetz . . . is destroyed and passes into a soil of a clearly podzolic character'. Other factors are important, but the fact that aspen dominates the vegetation suggests that its litter is active in producing the podzolic appearance of the soil. Popov also mentions that a similar phenomenon can be seen under birch in Siberia.

Similarly, on the 'bluff podzols' and grey wooded soils of central Canada, aspen is an important constituent of the vegetation, along with spruce, birch, &c. These soils have attracted much attention since they are frequently alkaline or only slightly acid in the upper horizons, although extensive leaching of iron and aluminium, apart from clay as such, has taken place. (See Nygard *et al.*, 1952, and Williams and Bowser, 1952, for recent accounts and earlier references.)

Somewhat comparable podzolic soils have been described in Eire by Gallagher and Walsh (1942). These soils have developed on calcareous drift and occur under a grass cover; the reaction of the solum is alkaline, *c.* pH 8.

No chemical data was given by Popov, but the grey forest soils of Russia may develop quite strongly bleached surface horizons at only slight acidity. These nearly neutral soils have posed a problem to the soil chemist, for it has long been assumed that podzolization can only develop under acid conditions. In the light of the previous papers of this series it has become obvious that the extracts of leaf material have an appreciable activity even at pH 7 and over, and in view of the field evidence mentioned above it seemed probable that an investigation of the properties of aspen leaves would provide interesting results.

Since the aspen was the first broadleaved species to be reported in this study, it was felt desirable to describe a parallel investigation on some other deciduous type for the purpose of comparison. The ash (*Fraxinus excelsior*) was chosen since it is not known to cause podzolization, and it normally grows on soils of high base saturation, which in Britain are of the Brown Earth type.

Experimental

Autumn fallen ash and aspen leaves were used throughout this work. The leaves were collected at sufficiently short intervals to avoid leaching by rain; each batch was dried at 50° C. immediately after collection and finally ground to a fine powder.

The experimental details of the methods used in this study were the same as described previously. Five per cent. water extracts of the dry leaves were used throughout.

Effect of pH and aeration on the solution of ferric and aluminium hydrous oxides

The results obtained in this experiment are given in Fig. 1. All the solutions gave positive reactions for ferrous iron when tested with dipyridyl, but quantitative determination of the ferrous iron was prevented by the coagulation of organic matter on addition of the acetate buffer.

The figure shows that under anaerobic conditions the aspen is very effective in dissolving ferric oxide both at pH 5·1 (the pH of the leaf extract) and at pH 7·2. Indeed, the extent of the solution was only reduced some 10 per cent. by the increase in alkalinity. It can also be seen from the figure that the ability of the aspen extract to dissolve ferric oxide is considerably reduced under aerobic conditions, particularly at the higher pH.

With respect to the ash, it is surprising that, contrary to what would be expected from the field evidence, the solution of iron and aluminium by the extract is quite appreciable. Raising the pH to near neutrality causes a marked decrease in the solution effect, even in the absence of oxygen; under the most adverse conditions, however, the effect is not negligible.

Solution of aluminium oxide by the two extracts exhibited no unusual features; as the extent of solution was approximately the same in each case, only the curves for the aspen are reproduced.

Reoxidation of ferrous-aspen and ferrous-ash solutions

The ferrous solutions, prepared anaerobically by treatment of ferric oxide with the extracts, were subjected to atmospheric oxidation. It was found that during the preparation of the ferrous-ash solution the pH rose to 6·7 and consequently reoxidation at this value alone was considered. Oxidation of the aspen solution was investigated at pH 5·0 and 7·0, sodium hydroxide being used to adjust the pH in the latter case.

As before, ferrous iron could not be determined quantitatively and consequently only the total iron remaining in solution was determined. The results are given in Fig. 2, which shows that, as would be expected from the previous experiment, at pH 7 oxidation-precipitation of the ferrous-aspen and ferrous-ash complexes takes place readily. As with the conifer extracts, part of the iron remains in solution after prolonged aeration, even at pH 7. At pH 5·0, the aspen solution is comparatively stable, precipitation being relatively slight.

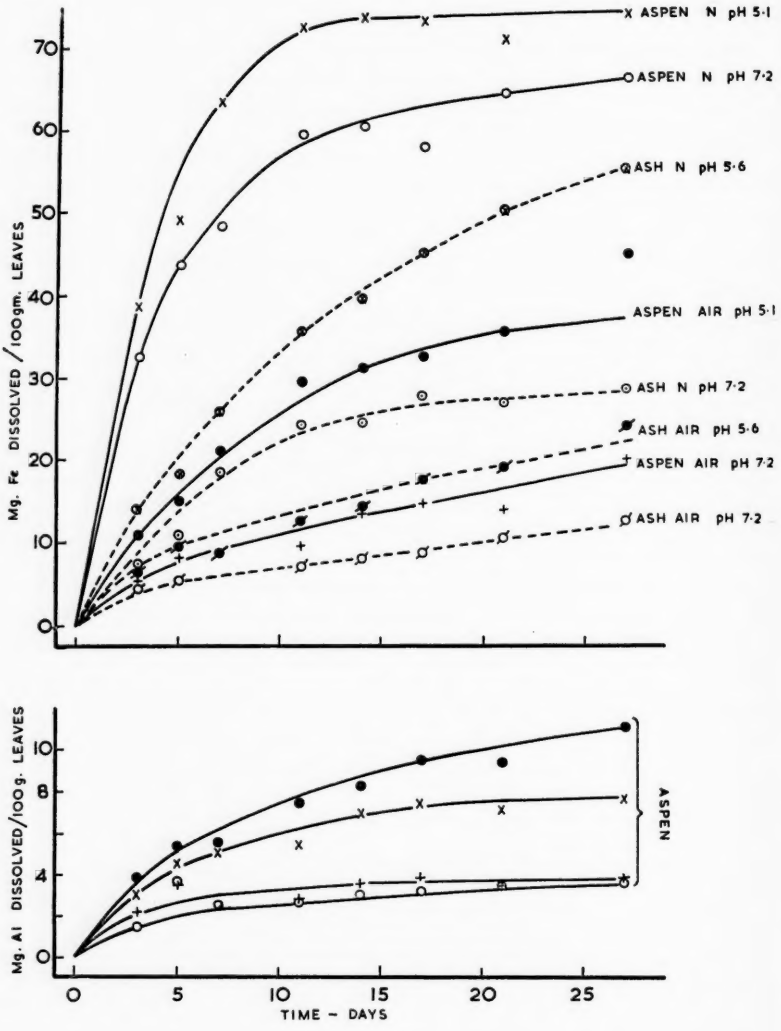

FIG. 1.

Variation of the solubility of iron and aluminium with pH

The iron and aluminium solutions used for these determinations were prepared from the oxides as in the previously reported experiments. As before, calcium hydroxide was used to adjust the pH. The results are given in the table below.

Aspen			*Ash*		
	mg./l. retained in solution by 5% leaf extract			*mg./l. retained in solution by 5% leaf extract*	
pH	*Fe*	*Al*	*pH*	*Fe*	*Al*
4·7	15·4	..	6·5	12·0	..
6·0	10·1	..	8·0	7·4	..
8·0	7·9	..	..	..	..
			5·6	..	4·6
4·9	..	6·9	6·0	..	5·0
6·0	..	7·2	8·0	..	3·9
8·0	..	6·2	..	..	..

Although the iron values are considerably lower than those obtained with the conifer extracts, they exceed the values which would obtain in an ionic system, thus indicating complex formation. The aluminium figures indicate a comparatively small stabilizing influence by the extracts.

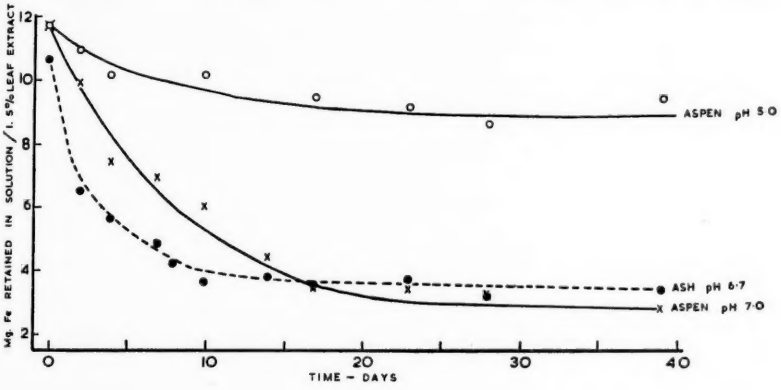

FIG. 2.

Water-soluble calcium and magnesium contents of ash and aspen leaves

In the preceding experiments, when preparing samples of the extracts for analysis, the formation of a copious white precipitate on the addition of sulphuric acid indicated that the leaves contain appreciable amounts of water-soluble calcium compounds. This observation was of considerable interest in view of the generally high percentage base saturation found under ash and in the soils of the grey wooded soil regions. The total and water-soluble calcium and magnesium contents of the leaves were therefore determined.

Approximately 5-g. samples of the leaves were dried to constant weight at 105° C., extracted overnight with 200 ml. of distilled water, and filtered; the leaves were then washed on the filter with approximately 50 ml. of water. The combined extracts and washings were evaporated with nitric-perchloric-sulphuric acids, to destroy organic matter, and the calcium and magnesium determined gravimetrically after precipitation

as the oxalate and ammonium phosphate respectively. The total calcium and magnesium contents were determined similarly on ashed samples, after evaporation with hydrofluoric acid and fusion with potassium bisulphate. The results given below are expressed as percentage oxide in the oven-dry leaves.

	Aspen		*Ash*	
	CaO %	*MgO* %	*CaO* %	*MgO* %
Water soluble . .	0·9	0·4	3·6	0·6
Total . . .	4·2	0·5	6·0	0·7

Discussion

The effectiveness of the aspen extract in dissolving ferric oxide at pH 7 indicates that the process of iron mobilization is not one of acid solution *per se*, or even necessarily associated with a low pH. The ability of the aspen to mobilize iron at an alkaline reaction must be attributed to the presence in the leaves of substances capable of forming with iron a complex which is stable at high pH values.

The high water-soluble calcium content of the aspen and ash leaves at once suggests an explanation for the high percentage base saturation, and hence the high pH commonly observed under these trees. It seems reasonable to assume that additional calcium would be rendered soluble during decomposition of the leaves, so that in all probability the values quoted for the water-soluble calcium represents an underestimate of the true position. In support of this contention the results may be quoted of some recent work on the properties of leachates of leaves decomposing under natural conditions (Lutwick *et al.*, 1952). This work shows that for a number of deciduous species, including aspen, the pH, total solids, ash content, and alkalinity of the ash of the leachates vary considerably throughout the year. In general an initial sharp decrease in the properties mentioned is followed by an equally sharp increase, which is in turn succeeded by a rather slower decrease. Presumably the calcium content of the leachates follows the same pattern.

Krakov has determined the water-soluble calcium and magnesium contents of various plant types, and a selection of his results are quoted below (Glinka, 1931).

	CaO (*g. per kg. dry matter*)	*MgO*
Oak	0·96	1·52
Birch	0·84	0·98
Aspen	2·13	1·13
Pine	0·14	0·33
Spruce	Trace	0·15
Fir (*abies*)	,,	0·24

The values for the conifers are thus considerably lower than those for the deciduous types, particularly the aspen. Base desaturation and acidification may be considered as essential characteristics of a podzol

developed under conifers, while the grey-brown podzolic, grey wooded, and brown forest soils developed under broadleaved species are commonly base saturated, or nearly so. These groups of soils thus reflect in a marked way the base content of the water extracts quoted above.

It is difficult to reconcile the comparatively extensive solution effect of the ash leaf extract with the absence of podzol development under ash trees. The soluble calcium present in the ash leaves presumably tends to maintain the pH value of the soil at a reasonably high level, and this would tend to limit the solution of sesquioxides, since the activity of the ash extract is decreased by raising the pH (Fig. 1). Nevertheless, it must be admitted that on the basis of the laboratory results one would expect the ash to be a fairly effective podzol former.

In a recently published note (Schnitzer and DeLong, 1952) it has been stated that leachates produced in the field by natural rainfall from deciduous leaves and conifer needles exhibit the same general properties as the laboratory preparations described here. It does not, therefore, seem open to doubt that the solution-reduction processes described here must operate in the soil to some extent, so that it can only be concluded that a counteracting process must operate to prevent podzolization under an ash cover. (It may be noted that this problem is not confined to the ash alone, since of the several other broadleaved species which have been examined in the course of the present study, none failed to produce some solution-reduction effect.) This suggests that although no signs of sesquioxide movement are observed under ash, for example, nevertheless a cycle of mobilization and immobilization exists which results in no net translocation of the oxides.

In this discussion the word podzolization has been used simply in the sense of a bleaching of the A horizon. Robinson (1949) considered that grey-brown podzolic soils were akin to the brown earths, and Muir (1949) has pointed out the close chemical similarities between the grey-brown podzolic, grey wooded, and the Russian grey forest soils. He also emphasized their differences from the podzol, a point recently stressed by Nygard *et al.* (1952). It would appear then that while a translocation of sesquioxides, and in particular iron, takes place in all members of the podzol and so-called podzolic soils, the mechanism in the two cases is not necessarily the same. This study has shown how even under alkaline conditions the sesquioxides may be mobilized and translocated, but further work will be necessary to explain fully the difference between the podzol group on the one hand and the podzolic group on the other.

An aspect of the soil-forming process that has not been considered in this work, and that may be responsible for counteracting the mobilizing action of the organic matter, is the action of the soil fauna in mixing and aerating the soil. In podzols earthworms are absent and the action of the soil fauna is confined to the raw humus; in brown earths, on the other hand, the activity of earthworms and other animals gives rise to a considerable turnover of soil material and organic matter and this would tend to counteract the bleaching of the upper horizons. In the case of the grey wooded and similar soils, it may be that the conditions are such as to restrict faunal activity.

Summary

1. Aqueous extracts of aspen and ash leaves have been found to react with ferric and aluminium oxides to form soluble metal-organic complexes. As with extracts of conifer needles, reduction of the ferric iron takes place under aerobic conditions.

2. In contrast to the conifers, the aspen extract retains its activity almost unimpaired at high pH values, which provides an explanation for the development of a strong A_2 horizon in certain neutral or only slightly acid soils.

3. The relatively high water-soluble calcium present in fallen aspen leaves is presumably responsible for the high pH and percentage base saturation of the grey wooded soils.

Acknowledgement

The author wishes to acknowledge his indebtedness to Dr. A. Muir for assistance with the Russian literature, and for much helpful discussion.

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THE STUDY OF SOIL STRUCTURE IN THE FIELD AND THE LABORATORY

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WITH FOUR PLATES

Summary

After defining the sense in which the term soil structure is used in the paper, the various methods for studying it are discussed, followed by a brief survey of recent literature. Descriptions are then given of adaptations of various methods which have been found suitable for studying structural changes in soils in long-term rotation experiments under the climatic conditions of Britain. As an indication of the usefulness of the methods, some results typical of those obtained in the field and laboratory are given.

THERE seems to be no generally accepted definition of soil structure, and in this paper that of Bradfield (1950) is used, who defines structure as 'referring to the arrangement of the solid particles in the soil profile'. Thus any process which alters the arrangement of the ultimate particles of the soil is altering its structure. On the basis of this definition there cannot be a structureless soil, a term which is frequently used, e.g. by Nikiforoff (1941).

On the arrangement of the soil particles, i.e. the structure, depend the water movement, water retention, aeration, &c., in soils. The ease of movement of roots also depends upon the structure. It is generally recognized that the physical condition of any soil type from these points of view is about optimum when old pastures are ploughed, relatively little effort being needed on the part of the farmer to produce the optimum state. From the agricultural point of view, farm operations and rotations should be designed to maintain this state. To develop methods for doing this necessitates defining, in both qualitative and quantitative terms, the physical attributes of any soil type in its optimum physical state, thus providing a standard for a soil type in a given area with which to compare arable land of the same type but of poorer structural condition, which requires improving. If satisfactory techniques for assessing structural state of the soil can be developed it should be possible to assess changes in arable and grassland from one year to the next.

In the field, as opposed to the laboratory, studies of soil structure have been largely descriptive and qualitative and have been concerned with (1) size and shape of aggregates,* (2) the size and shape of the pores and channels, and (3) properties resulting from the types of aggregates and their distribution. Agriculturally the changes in soil structure are largely concerned with the cultivated layer. Nevertheless, changes below this

* It is much more satisfactory to describe the size, shape, porosity, &c., of the aggregates rather than give names to them, more particularly because there is no generally accepted nomenclature.

do occur during crop rotations, but the structure below the cultivated layer appears to depend, primarily, on the soil type and to a lesser extent on cultivations and crops. The structure as seen in the field of the whole soil profile has been studied by a number of workers. Clarke (1941), Nikiforoff (1941), Gračanin (1950), and Frei (1950) have put forward tentative schemes for classifying soil aggregates in the field.

Quantitative methods for studying aspects of soil structure have been largely for use in the laboratory, although some have been for field use. They include the following:

Direct measurement of soil structure

From the definition this involves measuring size and shape of the aggregates and the space between them, i.e. a 3-dimensional study of undisturbed soil. This is very difficult. A number of workers (Harper and Volk, 1936; Redlich, 1940; Sideri, 1938; Day, 1948; and Kubiena, 1938) have developed techniques for cutting thin sections as for rocks, subsequently examining them with a petrological microscope.

Most measurements of structure are, however, indirect, and they can be placed into two groups:

(i) measurement of the size of the aggregates;
(ii) measurement of a soil property which is a function of the structure.

In addition there are a considerable number of laboratory methods for assessing the stability of a structure.

Measurement of size of aggregates

This has been done largely in the field using a set of sieves. Keen (1933) used four sieves, 1·5, 0·5, and 0·25 in. (square holes) and 3 mm. (round holes). One of the difficulties with this method is the tendency of many soils to ball in the process. Other workers include Cole (1939) and Russell and Tamhane (1940).

Measurement of a soil property which is a function of the structure

A number of measurements are possible, all being related to the pore space.

Infiltration or drainage rate of water into soil. This depends not on the structure of the surface soil alone but the zone below, and has to be determined in the field. The usual method is to place a cylinder in the soil and, after filling it with water, find the time for a given fraction to infiltrate. A criticism of such a method is that soil air tends to be trapped, so making conditions rather different from normal soil drainage. Numerous techniques have been suggested, e.g. by Marshall and Stirk (1950) and Musgrave (1935).

Percolation rate. This is the rate at which water passes through cores in the laboratory, the structure being as little damaged as possible during sampling. A fixed head of water is maintained. Bloodworth and Cowley (1951) and Uhland and O'Neal (1951) have developed methods. The same criticism applies to these methods as to those above. They are of less value than infiltration as the structure effect of the soil below 3–4 in. is missing.

To overcome these criticisms, methods for determining the drainage rate of soils under conditions more related to those found in the field have been developed (e.g. by Bendixen and Slater (1946), who have found the drainage rate of initially saturated soil under 60 cm. of water tension).

Total pore space. This is readily found, methods having been put forward by Russell and Balcerek (1944), Johnstone (1945), Perry (1942), and others. The total porosity is not of such value as the proportions of the total porosity occupied by air and water at field capacity. This is best obtained by taking cores of soil at field capacity for which Lutz (1949), Jamieson *et al.* (1950), Dortignac (1950), and others have suggested techniques.

In soil of good structure it is desirable to have a reasonable proportion, e.g. 10–20 per cent. of soil volume, of the total porosity in large pores readily drained at low tensions, e.g. 60 cm. of water with the remainder emptied at tensions less than 15,500 cm. of water (15 atmospheres).* Methods for studying porosity at different tensions have been developed by Haines (1930), Donat (1937), Bradfield and Jamieson (1938), and Childs (1940, 1942). The laboratory techniques of Leamer and Shaw (1941) and Jamieson and Reed (1949) are widely used.

For the determination of the pore space occupied by air in aggregates a method using Boyle's Law apparatus has been developed by Torstensson and Eriksson (1936) and modified by Russell (1949) for field use.

Rate of aeration, &c. The roots of growing plants require considerable quantities of oxygen. Unless the supply can be maintained the rate of uptake of nutrients, &c., is reduced. Taylor (1949), Raney (1949), Evans and Kirkham (1949), Wilde (1950), and others have developed techniques for studying gaseous diffusion, but under somewhat artificial conditions.

Degree of compaction. For vigorous plant growth it is essential that roots should be able to move readily in the soil, a property which is determined by the extent of its compaction. Quantitative methods for assessing compaction are based on the force required to push a probe into the soil (Davies, 1930, 1931, and 1933; Robertson and Hansen, 1950; and S. J. Richards, 1941).

Ease of cultivation of soil. The ease of drawing implements, such as ploughs, through soil is partly related to the pore structure, and can be measured with a draw-bar dynamometer.

'Available' soil water. The available soil water represents the difference between water content at field capacity and wilting-point and is largely determined by the pore-size distribution. Field capacity is best found by Viehmeyer and Hendrickson's (1950) method. For wilting-point there are various techniques (e.g. Briggs and Shantz, 1912; Furr and Reeve, 1945; Richards and Weaver, 1944; Schofield and Da Costa, 1935; and Lehane and Staple, 1951).

Measurement of the probable stability of a structure

The stability of the structure resulting from the cultivation of arable land resides in the aggregates. The more resistant they are to wetting

* It is not suggested that this 'ideal' condition is possible in practice.

and drying, freezing and thawing, the less likely is the surface of a soil to become panned as a result of the breaking down of the aggregates.

Techniques for studying stability include:

Wet-sieving soil aggregates. There are many variations in technique, e.g. the soil may be initially at field-moisture or air-dry. It may be wetted by covering with water, by standing on moist filter-paper at a low tension, by spraying gently, by wetting under vacuum, &c. After wetting it may be shaken or stirred, or neither. The aggregates are then sorted on one or more sieves of varying size. The sieves may be kept under water all the time or brought out at each upward and downward movement. The sieving may be by hand or by machine. The method appears to have originated with Tiulin (1928). A widely used modification is that of Yoder (1936).

Subjecting aggregates to the impact of falling water droplets simulating the action of rain. This was originally put forward by McCalla (1944). It has been modified by Smith and Cernuda (1951) and others.

Rate of breakdown of the air-dry aggregates on wetting. A very simple method requiring little equipment and providing quite a good guide to field behaviour has been put forward by Gračanin (1950).

Permeability of a column of air-dry aggregates to water. The stability of the aggregates to wetting determines the speed at which water will continue to flow through a tube packed with them. This method of assessing structural stability has been used in recent years by Hénin and Turc (1949).

Extent of dispersion of the silt and clay fractions in soil. In a soil of good structure little or none of the clay and silt fraction is unaggregated. A method for measuring this proportion has been put forward by Middleton (1930). Somewhat similar methods were used by Kolodny and Neal (1941), Clarke and Marshall (1947), Puri and Keen (1925), and others.

This is a very brief summary of some of the methods used in studying phenomena related to soil structure. There are no accepted techniques. Most of the work concerns soil problems in continental climates. At Jealott's Hill during the last 9 years we have been examining and modifying techniques appropriate to a maritime climate that could be used for studying physical changes in long-term rotation experiments, &c. The descriptions of the techniques which we are using are illustrated with some results to give an indication of their usefulness.

Direct measurement of soil structure

Soil samples have been impregnated with Santolite (Monsanto) and thin sections cut using the standard technique for rock samples. Soil samples, as near $1 \times 1 \times 1$ in. as possible, have had one surface ground on medium sandpaper and then heated in Santolite for $1\frac{1}{2}$ hours at 90° C. After cooling the surface was ground with carborundum, the sample returned to Santolite for 30 minutes, then mounted on a slide and ground until less than 1/1,000th of an inch. It was then mounted in Canada balsam.

It has been found possible with this method to cut sections in soils with a very high coarse-sand content.

Measurement of a soil property which is a function of the structure

Drainage rate. The drainage rates of saturated soil cores under a fixed tension have been found. Cores 3 in. in diameter and 2 in. in height have been taken with a hammer-type core sampler (see Plate I) which is a modification of that developed by Lutz (1947). The samples are taken in tinned-iron sleeves fitted with slip-on lids, top and bottom. As far as possible, the samples are taken when the soil is at field capacity, as this provides further valuable data. The samples are weighed, wetted for 24 hours at 5 cm. tension, then slowly flooded, taking 2 hours. They are then removed, weighed, and the water drained in 30 minutes at 60-cm. tension found. The drainage has been carried out on sintered glass plates 90 mm. in diameter and ground flat (see Plate II). For tensions of 60 cm., plates of porosity '4' (pore diameter 5–10 μ) have been used, but for tensions between 300 and 800 cm. sintered glass plates porosity '5 on 3' (pore diameter 1–1·5 μ) and ground flat have been used. With cores taken from long-term fertility experiments, this procedure has been found to give useful results (see Table 1). With stony soils, however, the process of collecting cores has been time-consuming.

TABLE 1

Crop	*Treatment in year before wheat*	*Date of sampling*	*g. of water drained at 60-cm. tension from soil cores 3 in. diam. × 2 in. high*	
			After 15 minutes	*After 60 minutes*
Winter wheat	1 year fallow (after 3 years cereal)	April	5·3	6·6
,,	1 year ley (grazed) after 3 years cereal	,,	11·9	12·6

Pore space. The cores used for determining the drainage rate under fixed tension are also used for finding the moisture content and effective porosity at field capacity. By plotting against tensions the amount of water drained at, for example, 10, 30, 60, and 120 cm. of water, curves characteristic of different soils are obtained.

In some of our work we have been concerned with very stony soils which were unsuited to the core technique. In these cases the soil has been sampled in the field with a spade and put into a waxed container. In the laboratory clods have been taken about 4 cm. diameter, weighed quickly, then immersed in paraffin wax at 60° C., removed, and weighed. The volume has been found from the loss in weight when the clods were immersed in water. The moisture content was found on the sample after removing the wax coat.

An illustration of the type of data obtained is given in Table 2.

TABLE 2

Soil No.	*Description of soil*	*Percentage of total soil volume*		
		Pore space	*Volume occupied by water at field capacity*	*Volume occupied by air*
JH 76	Grassland, about 100 years old	61·0	39·0	22·0
JH 77	Part of above after 4 years cultivation	56·4	46·1	10·3
JH 79	After 4 years cultivation following 25 years grass	49·4	37·5	11·9
JH 81	Continuous arable within living memory	43·3	35·1	8·2

N.B. In all the above, the soil type was clay loam.

Degree of compaction. The degree of compaction has been studied using the instrument developed by Davies (1930, 1931, and 1933), and has been found to be quite well correlated with growth of cereals. Cultivation of soils when too wet leads to a structural state in which compactometer values are high when the soil becomes dry and the areas where these readings are obtained correspond with those of poor growth. In some instances (Table 3), however, very low compactometer readings on soils sown with kale have been found to coincide with areas of poor growth in dry weather, whilst areas of much better growth have had much higher compactometer readings. This has been attributed to rapid evaporation from the 'open' structured soil where the compactometer readings were low.

TABLE 3

Condition of crop	*Average force in lb. required to push probe 7 in. into soil*
Kale growing well	32
Poor kale	18

Ease of cultivation of the soil. Using a dynamometer developed by the N.I.A.E., measurements of the draw-bar pull have been made during the ploughing of fields of the same soil type but varying structural state owing to different rotations. The fields, all in wheat stubble, were ploughed on the same day to the same depth. A set of measurements was taken in the morning and another set in the afternoon. The values given are the means of a considerable number of 'runs'. The overall objective from an agricultural point of view in studying soil structure is its bearing on crop yields. The subsequent yields of oats following ploughing of the fields just referred to are given in Table 4.

'*Available*' *soil water.* With soils of the same type but following different rotations considerable differences in the amount of available water have been found. Field capacity has been determined by saturating the soil with water, allowing to drain for 48 hours after covering to

prevent evaporation, and then sampling for moisture-content determination. Wilting point has been found by the Sunflower method (Briggs and Shantz, 1912). An example is given in Table 5.

TABLE 4

Soil No.	*Description of field*	*Draw-bar pull (lb./sq. in.) when ploughed during winter 1952 (all measurements on same day)*	*Crop*	*Yield cwt./acre*	*Fertilizer treatment 1952*
JH 71	Arable for 4 years after *c.* 75 years grass	2,300–2,500	Oats (Spring)	32	1 cwt. I.C.I. No. 1 when drilled
JH 106	1 year arable after 5 years grass	3,200–3,300	,,	23	1½ cwt., ditto
JH 105	3 years arable after 5 years grass	4,200–4,500	,,	15	2 cwt., ditto

TABLE 5

Soil No.	*Description of soil*	*Volume of water in ml. per 100 ml. of soil (0–6 in.) at:*		*'Available' water*
		Field capacity	*Wilting percentage*	
JH 87	Ley for 2 years	19·9	7·3	12·6
JH 103	Old pasture	39·6	13·2	26·4

Measurement of the probable stability of a structure

Wet-sieving soil aggregates. At Jealott's Hill the original intention was to assess the size distribution of water-stable aggregates using a technique based on some of the characteristics of the method of Bouyoucos (1935) and also of Tiulin (1928). The field sample* was dried† at room temperature in the laboratory, the larger lumps gently broken, and a 50-g. sample taken. This was placed in 600 ml. of water in a cylinder, inverted once, and allowed to stand for 30 minutes. The cylinder was then completely inverted 30 times and the contents poured on to a 3-mm. round-hole sieve standing in a dish with sufficient water‡ just to cover the soil (in this case 600 ml. in a dish 33 cm. in diameter). The

* For studying aggregate stability, sampling with a spade has been found to be the most satisfactory method. When the study is to be conducted for a considerable period, e.g. some years, a site on the field is selected and an area 20–40 yards square is marked out. Holes are dug to the usual depth of cultivation and one face trimmed vertically. A slice 6 in. wide and 1 in. thick is cut and ⅓ on each side removed so that a slice 2 in. × 1 in. × depth of ploughing is obtained. This is repeated at four more points distributed uniformly over the area, the soil samples being placed immediately in an air-tight container. The process is repeated so that a measure of field-sampling error can be obtained.

The use of metal cylinders for sampling has not been found satisfactory in dry weather or with stony soils.

† The reasons for using air-dried soil rather than moist soil direct from the field are considered later.

‡ Distilled water was used first, but later tap-water, as it appeared to make no significant difference to the results.

sieve was raised out of the water and pushed back again 30 times in such a way that the aggregates were covered each time. The motion was not quite up and down but a little from side to side in order to move the aggregates gently to and fro across the sieve. All material that passed through was then transferred to a 1-mm. round-hole sieve and the process repeated. It was then repeated using a 0·252-mm. wire-mesh sieve.

The material remaining on the sieves was dried at 105° C. and weighed. The aggregates > 3 mm. were boiled in a beaker with 50–150 ml. of 6 per cent. H_2O_2 until the stones > 3 mm. were freed from the aggregated material < 3 mm. After resieving, the stones > 3 mm. were dried and weighed. This weight was subtracted from the total weight of oven-dry material, to give the weight of soil < 3 mm. originally in water-stable aggregates > 3 mm. This process was repeated on the other sieves. The results are expressed as the weight of water-stable aggregates > 3 mm. which would be present in 100 g. of oven-dry soil < 3 mm., i.e.

$$\frac{\text{Wt. of soil} < 3 \text{ mm. in water-stable aggregates} > 3 \text{ mm.}}{50 - \{\text{wt. of stones} > 3 \text{ mm.} + \% \text{ (water in air-dry soil/2)}\}} \times 100.$$

It has been found, however, that results from methods such as this are liable to vary considerably when the wet-sieving of the same soil is carried out by different people. The variations that can be found are illustrated by the data in Table 6.

TABLE 6

	The percentage of soil < 3 mm. in water-stable aggregates > 3 mm.	
Worker	*Soil No. J.H. 103*	*Soil No. J.H. 77*
1	15·8	14·4
2	19·1	10·6
3	20·7	13·1
4	19·2	14·2
5	27·7	16·8
6	30·1	15·5
7	30·3	19·6

Other factors have been found to influence the results, including the size and distribution of the air-dry aggregates. These observations led to doubts as to the value of determining the size-distribution of water-stable aggregates for a given soil. It was decided that it would be more satisfactory to compare the stability of aggregates of different soils sampled and prepared under carefully standardized conditions. A method has been developed in which personal factors have been eliminated as far as possible.

The preparation of the sample is of considerable importance. After bringing the sample in from the field and drying it at the temperature of the laboratory it is pushed through a $\frac{1}{2}$-in. mesh sieve. This material is then pushed through a 5-mm. round-hole sieve and the material

retained on a 3-mm. round-hole sieve is used as the sample for wet-sieving. A group of samples to be compared is then exposed to the atmosphere for 48 hours so as to attain as far as possible a uniform moisture content. The extent to which the humidity of the atmosphere can affect the water stability of the aggregates is illustrated in Table 7. Where comparisons are being made with soils over a period of months or years it is suggested that they should be maintained at a standard humidity for some days after preparation of the air-dried sample.

TABLE 7

Pre-sieving treatment	*g. H_2O per 100 g. oven-dry aggregates at time of sieving*	*Percentage of soil < 2 mm. in water-stable aggregates > 2 mm. (Soil No. J.H. 83)*
Left in dry atmosphere* for 18 days	0·96	15·96
Left in humid atmosphere† for 18 days	5·16	25·91

* In a desiccator containing silica gel. † In a desiccator containing water.

Fifty grammes of the prepared sample are then covered with 100 ml. of water at 18° C. and left for 30 minutes. It was then tipped in the middle of an 8-in. diameter 2-mm. round-hole sieve. A duplicate sample is prepared at the same time on another sieve. The sieves are raised and lowered mechanically (see Plate III) in water at 18° C. at 30 strokes per minute.‡ Samples of the same soil of fixed weight have been sieved for 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1,000 strokes and the results plotted. The curves tend to fall fairly sharply initially and then flatten out, but the number of strokes at which this takes place varies. At 500 strokes the curve is flattening for all soils so far studied; consequently this has been selected as a suitable number for routine sieving. Five hundred strokes have been found to bring out, satisfactorily, differences in the behaviour of the soils which can be correlated with observed differences in the field. Any number of sieves can be used, but two have been found satisfactory for much of the work—2-mm. and 0·5-mm.§ During the sieving operation each sieve is raised clear of the water at each stroke. In the modified method, using 2-mm. and 0·5-mm. sieves, the two sets of aggregates for each sieving are added together and boiled with 6 per cent. H_2O_2. The resieving is carried out on the two sieves simultaneously, and the stones > 2 mm. and sand < 2 mm. and > 0·5 mm. are collected separately, dried, and weighed. The results are expressed as before. It is considered that this method provides a measure of the water-stability of the aggregates.

The size fraction of narrow range (5–3 mm.) is sieved out because it has been observed that the initial size of the aggregates influences the amount retained finally during wet-sieving, and only by having the

‡ The machine is based partly on one developed by Dr. Peerlkamp at Groningen, Holland.

§ This is considered later.

aggregates within a narrow size range can this source of error be made reasonably small (Table 8). Somewhat similar observations have been made by Woodburn (1944).

TABLE 8

Initial size-range of air-dry aggregates	*Percentage of soil < 2 mm. in water-stable aggregates > 2 mm.*	
	Soil No. J.H. 103 Old pasture	*Soil No. J.H. 82 4 years arable following permanent pasture*
25–12·5 mm.	76	31·0
12·5–7 mm.	53	9·0
7–5 mm.	26	2·4
5–3 mm.	23	1·5

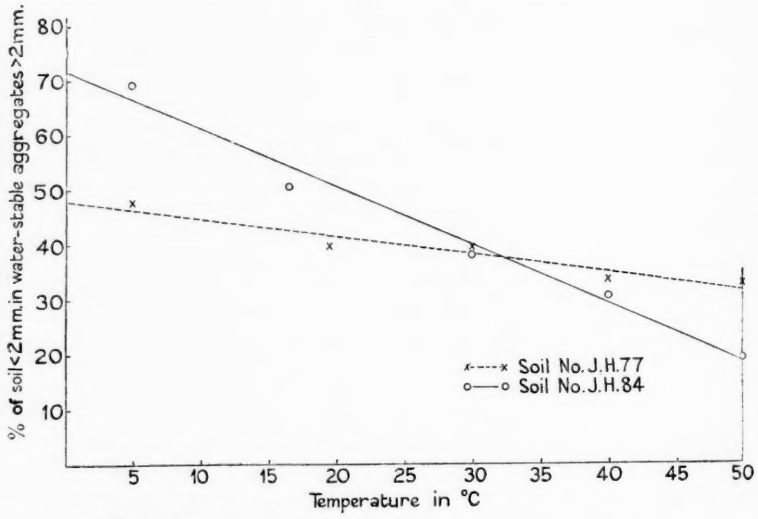

FIG. 1. Soil No. J.H. 77 (clay loam): $y = 48{\cdot}2 - 0{\cdot}331x$ ($\pm 0{\cdot}018$)
Soil No. J.H. 84 (loam to clay loam): $y = 71{\cdot}3 - 1{\cdot}056x$ ($\pm 0{\cdot}079$)

where y = % water-stable aggregates > 2 mm.
x = temperature of water in °C.

Standard error for single determination = $\pm 2{\cdot}2$. The regression of % water-stable aggregates > 2 mm. with temperature was significant for each soil.

The temperature of the laboratory and the water may vary considerably. It has been found necessary to soak and wet-sieve soils in water at a constant temperature (18° C.)* as the water stability of the aggregates varies with the temperature at which these operations are con-

* This temperature was chosen as it is the average laboratory temperature at Jealott's Hill.

ducted. The results for two soils over a fairly wide range of temperature are shown in Fig. 1.

Using the method of preparing and sieving the soil outlined above, it is possible to get quite good reproduction in the wet-sieving analysis. In Table 9 the results of wet-sieving soils taken from a rotation experiment are given. In each case, except rotation 1, the ploughing was at the end of the ley period.

TABLE 9

Rotations (5 course)	*Percentage of soil < 2 mm. in water-stable aggregates > 2 mm.*
1. Continuous arable	1·04±0·21*
2. 1 year ley followed by 4 years arable	3·75±0·28*
3. 2 years ley followed by 3 years arable	6·60±0·44*
4. 3 years ley followed by 2 years arable	9·76±0·72*
The differences between the 4 rotations were significant	

* The mean of 2 laboratory determinations on each of 8 composite field samples.

Examples of the standard error obtained in the determination of the water stability of air-dry aggregates from soils sampled twice a year for 9 years with two composite field samples each time are given in Table 10.

TABLE 10

Soil No.	*Description of soil*	*Sampling period*	*Average figure for % of soil < 2 mm. in water-stable aggregates > 2 mm.*	*Standard error*	
				Field sampling	*Laboratory determinations (single sample)*
J.H. 18	Old pasture (100 years)	Spring 1944 to Autumn 1952	74·7	±2·9	±1·3
J.H. 20	Ley established 1944		33·5	±3·4	±1·9

We have not found it satisfactory for purposes of comparison to wet-sieve soils immediately on bringing them from the field. Soils which are known from field observations to be quite different in physical behaviour can give very similar results on wet-sieving in a moist state, but very different values on wet-sieving after air-drying (Table 11). The fresh soils were sampled for wet-sieving after being brought in from the field. The remainder was air-dried before wet-sieving. Half the air-dry sample was sampled in the same way as the fresh soil and half by the standard way, i.e. crushing to pass a 5-mm. but retained on a 3-mm. sieve before wet-sieving.

TABLE 11

Soil No.	Percentage of soil < 2 mm. in water-stable aggregates > 2 mm.		
	Fresh soil	Air-dry soil	
		Sampling as fresh soil	< 5 > 3 mm. sample
J.H. 87	35·83	0·84	0·18
J.H. 103	43·18	23·05	17·78

The mode of wetting of soil greatly influences the results of wet-sieving. Figures for three different methods of wetting are given in Table 12. It is felt that laboratory assessments of soil structure and properties connected with it must at this stage of our knowledge make sense in terms of field observations. Wetting at 5-cm. tension did not differentiate between soils J.H. 67 and J.H. 81. From field observations it is clear that these soils behave quite differently when wetted and dried. Soaking the air-dry soil in water (method 1) gives results much more in line with field observations. Nevertheless, the small range in differences obtained by wetting under 5-cm. tension may be more in keeping with field behaviour of some soils under British conditions, and we have found it useful to use both methods of wetting and then consider the resulting data. Incidentally, the fact that the extent of aggregate break-down from wetting after evacuation (method 3) is more than that following slow wetting (method 2) suggests that the pressure of entrapped air may not be the major factor in the disintegration of air-dry aggregates on wetting. Russell and Tamhane (1940) found it necessary to wet evacuated soils by allowing a slow stream of air-free water vapour to pass over the soil for about an hour. This may have been more critical than the evacuation in deciding the stability of the aggregates.

TABLE 12

Method of wetting	Percentage of soil < 2 mm. in water-stable aggregates > 2 mm.		
	Soil No. J.H. 67	Soil No. J.H. 81	Soil No. J.H. 87
1. Soaking for 30 min. in 100 ml. water	31·27	12·82	0·69
2. Wetting for 5 hrs. at 5 cm. tension	84·84	85·77	42·44
3. Soaking in vacuum	35·15	16·86	1·60

The choice of sieve size is important. The majority of American, Russian, and other workers have used the percentage of water-stable aggregates from material < 0·25 mm. in aggregates > 0·25 mm. as their basis for comparison. Some have used the percentage > 0·1, or > 0·05 or > 0·02 mm. (see Browning *et al.*, 1943). A few have expressed results as percentages > 2 mm., e.g. Woodburn (1944) and Wilson and Browning

(1945). In studying changes in water stability of aggregates in old arable soils put down to grass since 1944 and using a range of sieves with aperture size from 0·25 mm. upwards, we have found that as the physical condition of the soil 'improved' under grass the percentage of water-stable aggregates between 1 and 0·25 mm. decreased and the percentage > 3 mm.* increased. Thus adding together the weights of these two sets of aggregates as would be done if the percentage $> 0{\cdot}25$ mm. were used tends to mask changes taking place in water-stable aggregation.

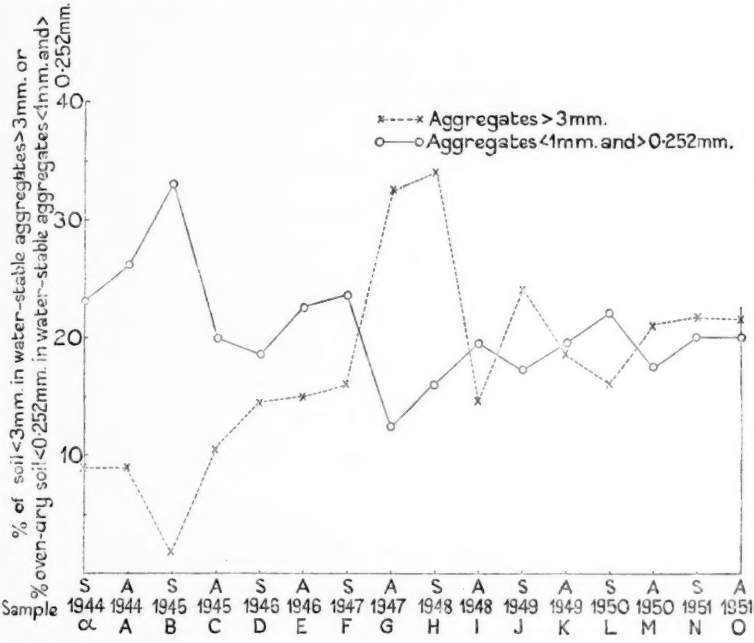

FIG. 2.

Fig. 2 illustrates the decrease in the smaller aggregates and increase in the larger over a period of years after an old arable soil had been put down to grass.

The amount retained on the 2-mm. sieve has brought out reasonably clearly differences observed in physical condition in the field, e.g. the extent to which soils have panned after heavy rain. The 2-mm. sieve has replaced the 3-mm. referred to earlier because with some soils the amount of material retained on the latter is small and the values for 'laboratory error' tend to be high. Where the aggregates are very unstable to wetting there is often very little soil retained on the 2-mm. sieve. In order to ensure a reasonable amount of soil a 0·5-mm. sieve

* This work was done before the change to 2- and 0·5-mm. sieves.

is used in addition. In Fig. 3 the percentage water-stable aggregates > 2 mm. and $> 0{\cdot}5$ mm. are plotted. For the old pasture the two graphs are very similar. For the ley the slope is a little steeper on the 0·5-mm. graph. Nevertheless the difference is about the same between 2-mm. and 0·5-mm. values at the last reading for both soils.

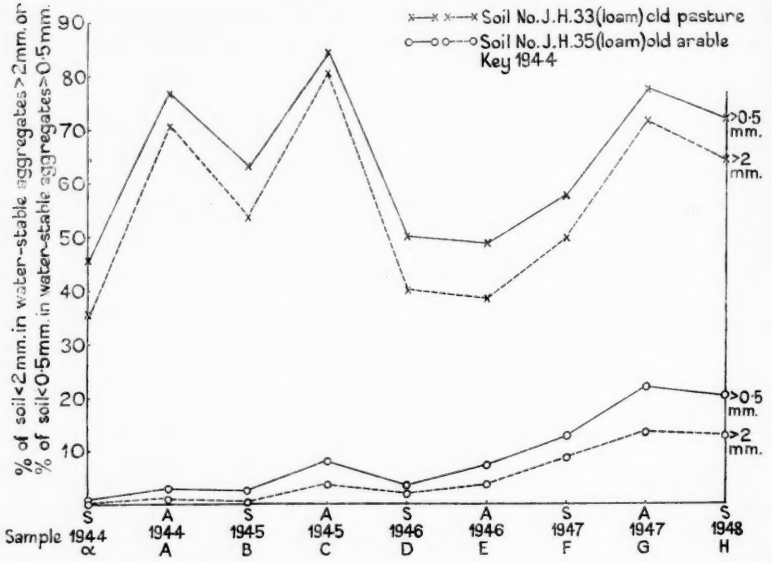

FIG. 3.

Subjecting aggregates to the impact of falling water droplets simulating the action of rain. Wet-sieving of air-dry soils is a highly artificial process. In the course of our observations it has been surprising, however, how often field observations of the behaviour of a tilth to weather changes, or variations in crop yield from one field to another, have been paralleled by laboratory measurements of the water stability of air-dry aggregates. It is nevertheless measuring a property of air-dry soil. It does not distinguish between soils when they are sampled moist and wet-sieved without air-drying. In the field one can conceive of at least two methods for aggregate breakdown when the temperature is above freezing-point: (1) slaking of the surface soil when air-dried; (2) mechanical disintegration of moist aggregates by rain drops. The gradual collapse of aggregates over a period of weeks in which the soil never dries out but is subject to intermittent periods of rain appears to be due largely to breakdown following the impact of falling raindrops.

A method which simulates the impact of raindrops on moist soil might therefore give useful information. A modification of the method proposed by McCalla (1944) has been developed. The average size of the large raindrops in western Europe is about 4 mm. diameter and they

have a terminal velocity of 7 metres per second. This means that there is about $8{\cdot}2 \times 10^3$ ergs per drop to be dissipated. Drops of water, mass 0·1 g. (which are approaching the maximum size possible for stability), have been allowed to fall 1 metre (K.E. at impact *c.* $9{\cdot}8 \times 10^3$ ergs) on to aggregates 4–5 mm. in diameter which have been wetted at a tension of 5 cm. Wetting at such a tension does not cause much disruption of soils even when they are very unstable to rapid slaking. The aggregate is placed in a small wire cage with a 3-mm. diameter round-hole aperture at the base. This cage enables excess water to get away quickly, but prevents the aggregate moving about (Plate IV). The number of drops required to break an aggregate so that it falls through the 3-mm. hole is then found. At least 20 aggregates must be taken from each soil sample. An illustration of the results which can be obtained by this method is given in Table 13, in which the soils used were the same as those for the wet-sieving data in Table 9. Both sets of results indicate the same trend in aggregate stability.

TABLE 13

Soil treatment (in 5-course rotation)	*Number of water drops. Mean of 20 determinations*
Continuous arable	11·6
End of 1 year ley	13·0
End of 2 years ley	15·0
End of 3 years ley	20·3

TABLE 14

Description of field	*Old arable, re-seeded Spring 1944, Soil No. J.H. 20*		*Old grassland Soil No. J.H. 18*	
Date of sampling	*% soil in water-stable aggregates or single particles* $< 50\ \mu$	*% soil* $< 50\ \mu$ *in water-stable aggregates* $> 50\ \mu$	*% soil in water-stable aggregates or single particles* $< 50\ \mu$	*% soil* $< 50\ \mu$ *in water-stable aggregates* $> 50\ \mu$
Spring 1944	15·09	80·16	6·82	90·61
,, 1946	8·98	88·19	4·70	93·53
,, 1948	8·52	88·80	4·94	93·20

Extent of dispersion of the silt and clay fractions in soil. One of the most noticeable characteristics, in the field, of old arable soils of considerable clay content is their sticky feeling when wet. This generally seems to disappear about 2 years after they have been put down to grass. This period appears to correspond to the aggregation of the smallest particles (possibly of free clay). This suggestion is based on a study of micro-aggregation, i.e. the proportion of the total silt and clay (material $< 50\ \mu$) that is in water-stable aggregates $> 50\ \mu$. There are various empirical methods of arriving at an estimate of this value. Soaking the soils in water for 24 hours followed by end-over-end shaking 30 times, then estimating the silt and clay in suspension by a pipette, has been

found reasonably satisfactory. The total silt and clay has been found by a separate determination after complete dispersion, using sodium hexametaphosphate.

One of the questions most frequently asked is to what extent the results of different methods of studying aggregate stability, &c., for groups of soils are correlated. The data in Table 15 can be considered reasonably typical of the results we have been obtaining.

TABLE 15

*Rotation on experimental plot**	*Grammes of water drained at 60 cm. tension after 60 min.*	*Number of water drops for breakdown of 5–4 mm. aggregates*	*% of soil < 2 mm. in water-stable aggregates > 2 mm.*	
			Wetted at 5 cm. tension	*Wetting by immersion in water*
Ley grazed, winter wheat, oats, barley	12·6	26·4	65·7	5·4
Fallow, winter wheat, oats, barley	6·6	19·3	64·0	2·23

* Plots sampled immediately before ploughing the ley in the autumn except for drainage cores which were sampled in the following spring.

There appears to be nothing absolute about the size of water-stable aggregates because as many different results can be obtained as there are variations in technique. The decision as to which particular technique to use must be guided by field observations which are relevant to the particular problem under study. In Table 15 it is seen that wetting at 5-cm. tension does not indicate much difference in water stability of the aggregates from the two treatments. The results obtained by wetting by immersion in water are much more in line with the field observations in these experimental plots. In many cases wetting by immersion of aggregates gives results which appear more in line with field observations of aggregate stability than wetting at 5-cm. tension, but there are instances when the results obtained by the latter method of wetting seem to be at least as reasonable in the light of field experiments.

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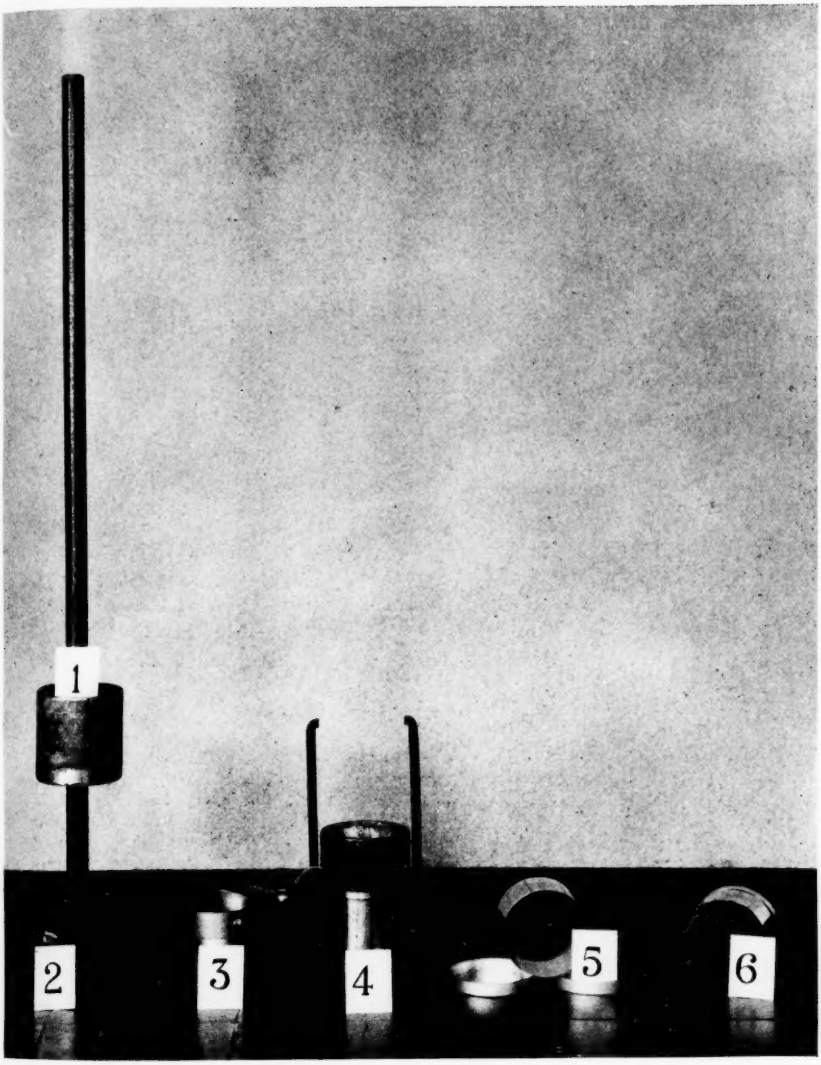
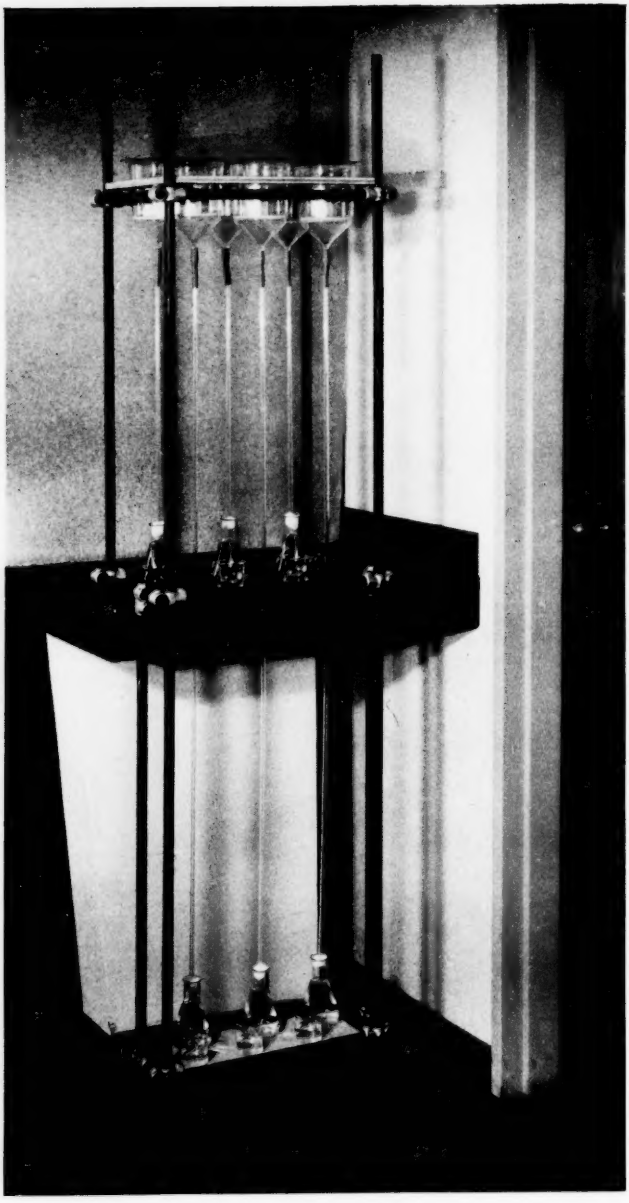
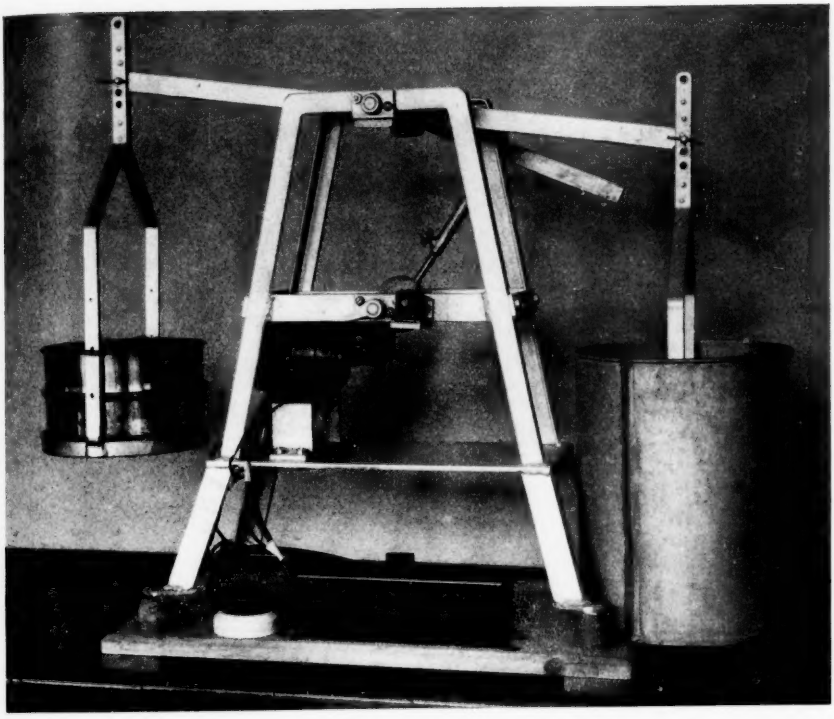


1 Sliding hammer (2·7 kg.)
2 Detachable head of cutting cylinder (3)
3 Cutting cylinder
4 Apparatus for extracting sleeve with soil cores from cutting cylinder
5 Tinned iron sleeves with slip-on lids
6 Soil core in tinned iron sleeves

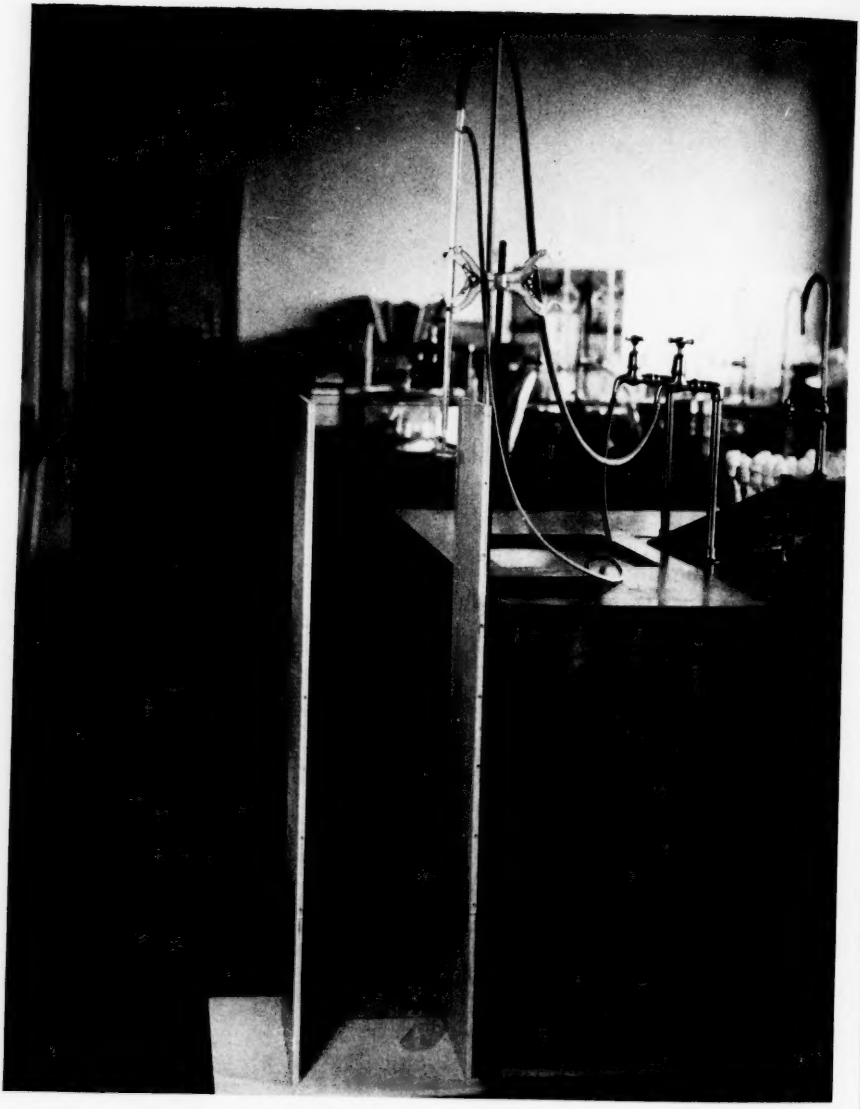
A. J. LOW—PLATE I



A. J. LOW—PLATE II



A. J. LOW—PLATE III



A. J. LOW—PLATE IV

SOIL STRUCTURE IN RELATION TO SOIL SUCTION (pF)

D. CRONEY AND J. D. COLEMAN

(Road Research Laboratory, Department of Scientific and Industrial Research)

INFORMATION on some aspects of soil structure can be obtained from a study of the suction or moisture-retaining characteristics of the soil. In this connexion, investigations into the relationship between suction (pressure less than atmospheric of the pore water) and moisture content have been made by Haines, Keen (1931), Schofield (1935), and others using both artificial and natural materials. More recently, at the Road Research Laboratory of the Department of Scientific and Industrial Research, methods based on the suction/moisture content relationship have been developed for estimating the moisture distribution beneath road and airfield foundations (Croney, 1952). This work has involved a considerable study of the suction properties of soils and other natural porous materials. Some of the results may be of interest outside the purely engineering field, although the curves given refer to tests on sub-soils.

The methods used for studying the suction/moisture content relationship, the suction plate (pF 0–pF 3), the centrifuge (pF 3–pF 4·5), and the vacuum desiccator (pF 5–pF 7), have been described in a recent paper (Croney, Coleman, and Bridge, 1952). A rapid method for measuring suction which involved no appreciable change of moisture content during the measurement was required for some of the work. For this purpose a modification of the suction-plate technique as shown in Fig. 1 was used. On placing the sample in contact with the porous plate, the water meniscus in the flow-tube tends to move towards the soil. Its position is, however, stabilized by adjusting the suction applied to the open end of the flow-tube. When the meniscus is observed through a microscope, and a rapidly adjustable mercury head is used to change the applied suction, measurements can be made without any appreciable displacement of the meniscus. This method is applicable only to suctions between pF 0 and pF 3, but a combined suction-plate and pressure membrane apparatus working on a similar principle was used for suctions between pF 3 and pF 3·6 with moderate success.

Some aspects of the work are reviewed below in relation to the three groups into which soils can be broadly classified from the point of view of their engineering properties. These groups are:

1. Incompressible soils, which include sands and materials like chalk and limestone. In soils of this group internal pressures arising from foundation loads or overburden are transmitted by intergranular contacts and do not contribute materially to the pore-water pressure. The volume of such soils is independent of the moisture content.
2. Fully compressible soils, which include all heavy clays. Under field conditions such soils are normally saturated, and foundation and overburden pressures are carried exclusively by the pore water.

A reduction of moisture content is accompanied by an equivalent decrease of volume.

3. Partially compressible soils, which include silty and sandy clays. Applied pressures are carried partly by intergranular contacts and partly by the pore water, and the materials exhibit some shrinkage when the moisture content is reduced.

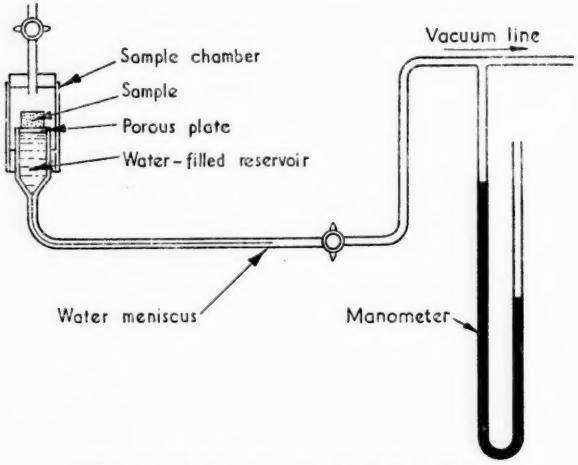


FIG. 1. Method of measuring soil suction.

Incompressible soils

Fig. 2 shows the suction/moisture content relationships for samples of soft (upper) and hard (lower) chalk, between saturation at zero suction and oven-dryness. The difference between the saturation moisture contents of the two materials may reflect the effect of consolidation pressure during the formation of the chalk beds. For both samples, as the suction applied to the initially saturated material is increased, no appreciable change of moisture content occurs until a suction of about pF 2·8 is reached, when air enters the structure. A decrease of moisture content occurs as the suction is further increased until the samples are virtually dry at pF 4·5. The suction at which air first enters is rather lower for the soft chalk than for the harder variety, confirming the difference between the average pore size of the two materials. At suctions above pF 3·6 the curves are practically identical for both samples. In this range the whole of the water present is probably contained in the 'breathing' channels perforating the shell-like material of which the chalk is constituted. The size of these channels would be unaffected by consolidation, and similar curves would be expected over this suction range.

For both samples of chalk there is a marked hysteresis between the curves corresponding to the wetting and drying conditions. This hysteresis probably arises in materials of this type from the degree of

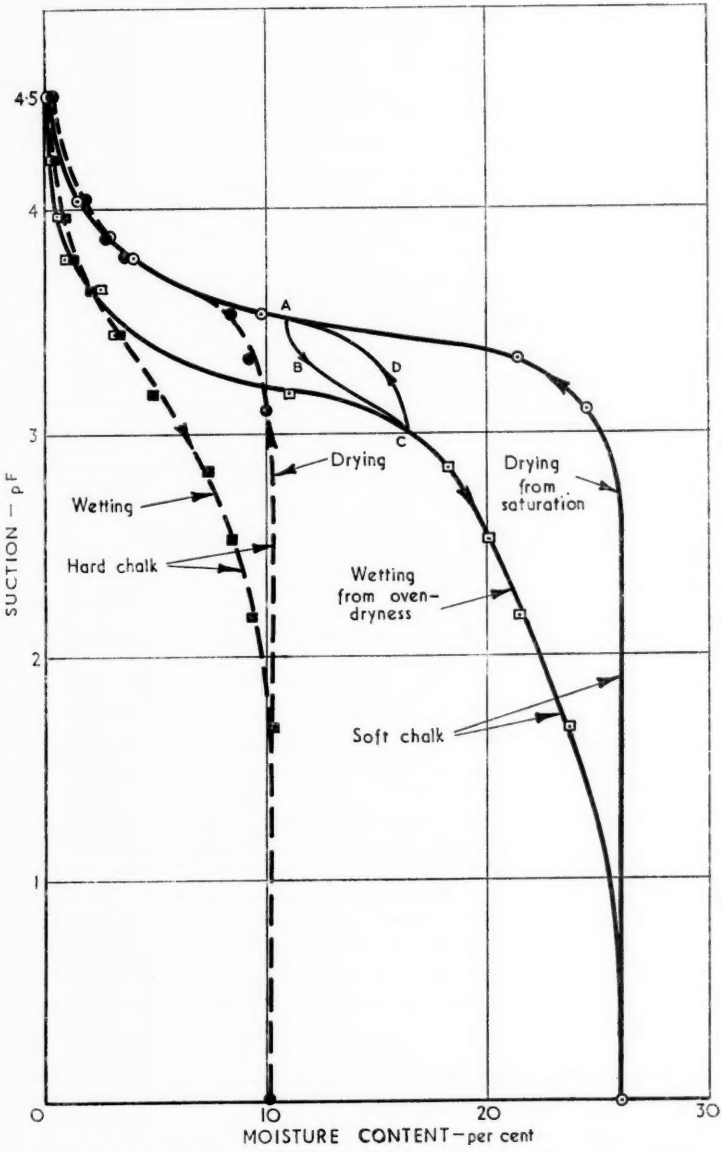


FIG. 2. Relationships between suction and moisture content for samples of hard and soft chalk.

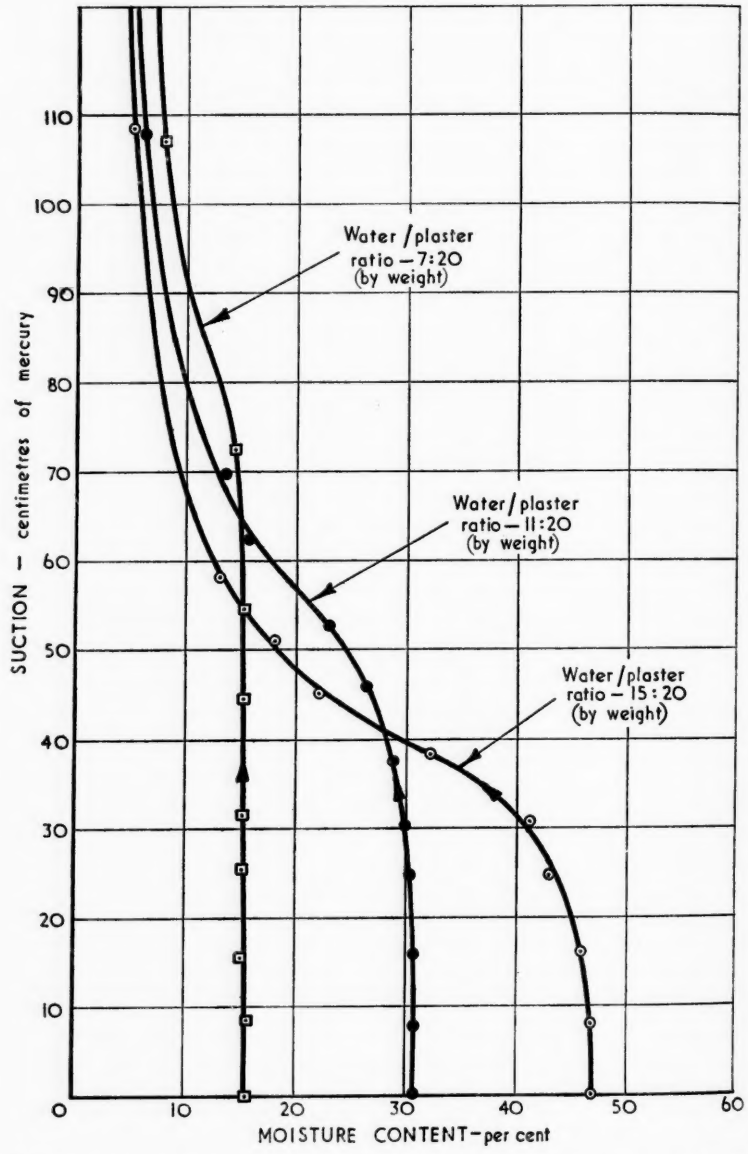


FIG. 3. Relationship between suction and moisture content for three mixes of plaster of Paris: drying condition.

control which the smaller pores exert on the suction at which the larger pores release their moisture as the suction is increased. Thus water is retained in large pores at suctions much greater than those at which the same pores will refill during the wetting process.

To show the type of result obtained with more controllable materials of the same kind, experiments were also made with plaster of Paris.

Fig. 3 shows the relationship between suction and moisture content for samples of plaster of Paris made to different water/plaster ratios. Drying curves only are shown (saturation to air-dryness), and the suction is in this instance expressed on a linear scale. The effect of the water/plaster ratio on the pore size of the plaster after setting is reflected in (*a*) the increase in the saturation moisture content, and (*b*) the decrease in the value of suction at which air first enters the structure, both of which occur as the water/plaster ratio is increased.

The structure of soil, as distinct from materials of rigid structure, can be modified either by disturbance or compaction. Curves of a similar type to those shown in Fig. 3 are obtained when incompressible soils, compacted to different initial dry densities, are dried from saturation. In such soils, increasing the dry density modifies the pore-size distribution and causes (*a*) a decrease in the amount of water held at low suctions, (*b*) an increase in the suction at which air first enters the soil as the suction is increased from zero, and (*c*) an increase in the amount of water held at high suctions. These points are illustrated in Fig. 4, which shows the suction/moisture content relationships for a silty sand at two dry densities. As might be expected from the above discussion, compacting the soil has the effect of partially closing the hysteresis loop between the wetting and drying curves.

Fully compressible soils

When the suction of a compressible soil is increased from zero, the reduction of moisture content which occurs may reflect either (*a*) shrinkage of the soil, which causes some modification of the soil structure, or (*b*) the entry of air, as in incompressible materials. The moisture content at which air enters the soil can be determined from shrinkage tests.

Fig. 5 shows the suction/moisture content relationships for a heavy clay soil (London clay). Curve *A* represents the 'undisturbed' material drying from a suction close to zero. Inset is shown the shrinkage curve for the soil drying from the field-moisture condition. The saturation line based on measurements of particle specific gravity shows a small air content at low suctions. This air is probably contained in surface irregularities and fissures. As the suction is increased air enters the structure when the moisture content falls to about 22 per cent., corresponding to a suction of about pF 4. Below this suction the pores are saturated and any change of moisture content is accompanied by an equivalent change of volume. Increases of suction above pF 4 cause only limited decreases of volume, since moisture is largely replaced by air.

If the drying process is continued to oven-dryness and the suction is then decreased, the wetting condition of the soil over the range pF 1–pF 7 is represented by the curve *B*, Fig. 5. On wetting to pF 1 the

moisture content of the soil is appreciably lower than its value prior to oven-drying, showing that some irreversible structural change has occurred as a result of oven-drying. On drying for a second time to pF 7 the suction relationship follows curve *C*, which forms a closed loop with curve *B*. Any subsequent wetting and drying cycles over the range pF 1–pF 7 give suction curves corresponding to this loop, which appears therefore to be unique for the soil.

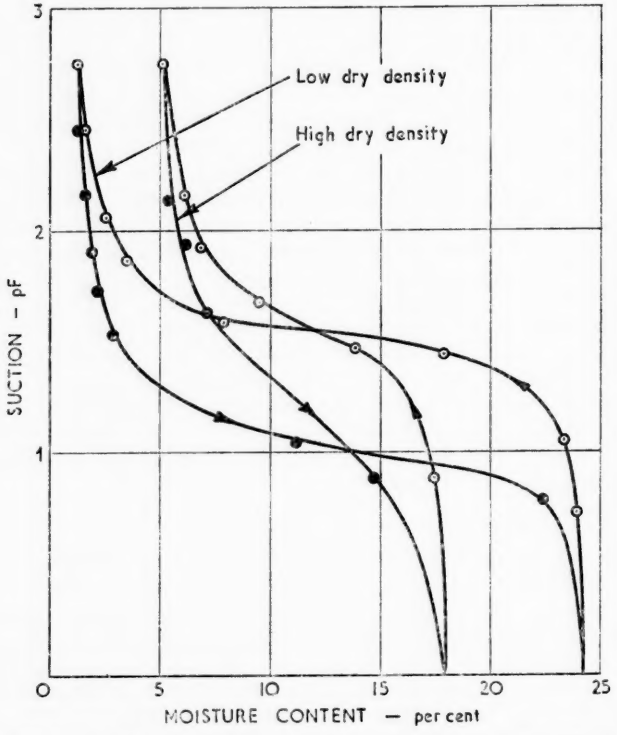


FIG. 4. Relationships between suction and moisture content for a silty sand at two densities.

When the structure of the clay is partially destroyed by thoroughly slurrying the soil at a high moisture content, and the slurried clay is subjected to an increasing suction, pF 0–pF 7, curve *D* is obtained. This curve joins the drying curve *A* at a suction of about pF 4·8, and at higher suctions is coincident with that curve. The moisture content held at any suction is clearly a function of the state of disturbance of the soil and may have any value between the limits determined by the curves *B* and *D*. The 'undisturbed' natural condition does in fact represent the state of disturbance which has arisen from natural disturbing processes, and the value of suction pF 4·8 at which the curves *A*

and *D* coalesce gives some indication of the pressures to which the clay has been subjected during its geological history. If the slurried soil is dried to a suction less than pF 4·8 and the suction is then reduced progressively and subsequently again increased, closed hysteresis loops of the type *E* and *F* are obtained. It follows that during the drying process a continuous and irreversible modification to the structure of the soil

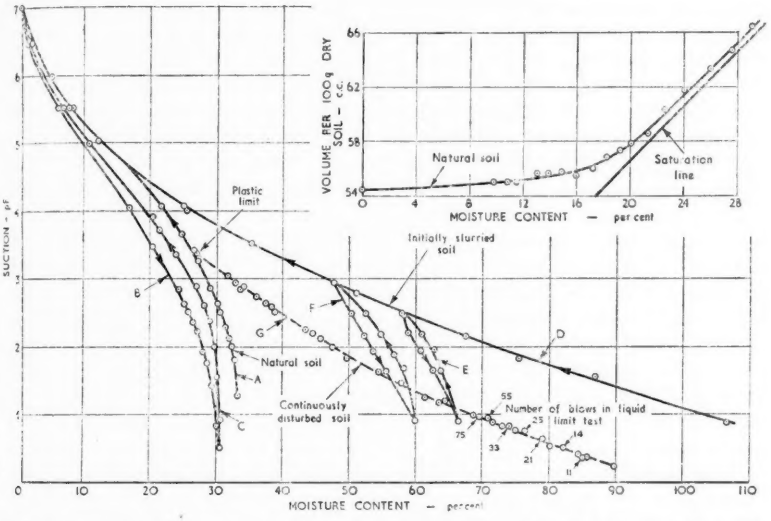


FIG. 5. Suction/moisture content and shrinkage relationships for a heavy clay soil.

occurs. If, however, the drying process is stopped when the suction has a certain value, any further fluctuations of suction lower than that value will not cause a further permanent change in the structural condition of the soil.

During the last few years several workers have attempted to ascribe pF values to the Atterberg limits. The obvious method of determining first the moisture content corresponding to the liquid (upper plastic) and the plastic (lower plastic) limits, and secondly the suction/moisture content relationship for the soil drying from the slurried condition, is not valid since the soil is in an entirely different structural condition during the two independent tests. At the Road Research Laboratory suction measurements have been made, using the rapid method already referred to, on actual samples used in the determination of the liquid and plastic limits. This investigation led to rather surprising results. The heavy clay soil referred to in Fig. 5 was thoroughly slurried with water to a moisture content well above the liquid limit. The number of blows required to close the groove, the suction of the soil immediately after the test, and the moisture content were all determined. This procedure was repeated a number of times with the soil drying until more than

100 blows were required to close the groove in the soil. Before each test the soil was thoroughly mixed in accordance with the standard procedure. The suction/moisture content points for various numbers of blows are shown in Fig. 5. The suction of the plastic limit was also determined, in this case with the combined suction-plate and pressure membrane apparatus. The liquid and plastic limit points were found to lie on the continuous dotted line, *G*, Fig. 5.

It was subsequently found that if the soil was disturbed without change of moisture content irrespective of its initial suction, it assumed a suction given by curve *G* at that moisture content. Most of the points shown on curve *G* were obtained by disturbing slurried samples which had been allowed to dry to points on curve *D* before being disturbed, or by disturbing natural samples whose suction/moisture content condition was represented by points on curve *A*. Further tests on samples in which the moisture content was progressively increased also gave suction/moisture content points on curve *G*, showing that it was a unique curve for the soil irrespective of whether the soil was wetting or drying. The broad conclusion is that if the suction/moisture content relationship of the soil is represented by a point above the line *G*, disturbance causes a decrease in suction to the value given by the line at the moisture content of the sample. On the other hand, if the initial suction is represented by a point below line *G*, disturbance will be accompanied by an increase of suction. Tests on other heavy clays have shown that for each soil there is a unique suction/moisture content relationship.

The physical significance of the above results has not yet been fully considered. It would appear, however, that in the field, disturbance of the soil referred to in Fig. 5 would in most cases render the moisture more readily available. In the application to civil engineering the curve *G* may be of importance as representing the suction of the soil during shearing.

Partially compressible soils

The relationship between suction and moisture content for partially compressible soils takes a form intermediate between the relationships for rigid materials and undisturbed fully compressible soils. The initial approximately vertical portion apparent in the drying curve for incompressible soils is absent, as also is the sharp 'turn over' corresponding to the sudden entry of air as the suction is increased. On the other hand, the slope of the drying curve is steeper than for fully compressible clays.

Fig. 6 shows the drying curve (curve *A*) of the suction/moisture content relationship for an 'undisturbed' sample of a silty clay. The shrinkage curve which is shown inset indicates that air enters the soil continuously as the suction is increased. Curve *B* shows the suction/moisture content relationship for initially slurried soil as the suction is increased from zero. For this soil a unique relationship between suction and moisture content, curve *C*, was found for samples after disturbance. Tests on a sandy clay soil showed a similar unique relationship for the disturbed samples. It was further found that the suction corresponding

to the intersection point of the relationship representing the disturbed soil with the drying curve for the natural 'undisturbed' material was much lower for light soils than for heavy clays. Thus for the sandy clay this point corresponded to pF 1·4, for the silty clay pF 2·6, and for the heavy clay pF 3·4.

The soil scientist interested in agricultural soils is naturally mainly

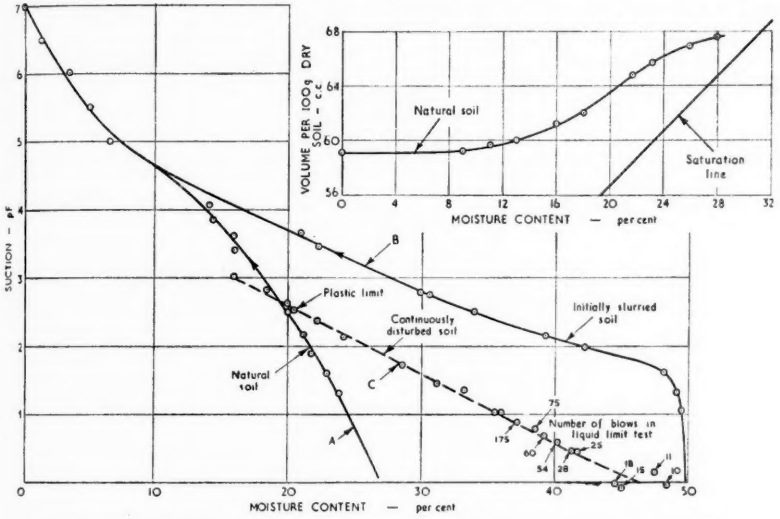


FIG. 6. Suction/moisture content and shrinkage relationships for a light clay soil.

concerned with intermediate soils. The structural condition of such soils will, as for the heavy clays, be reflected in the suction relationships. Although it is only in the simplest cases that an analysis of the suction curves alone gives a complete picture of the soil structure, the effect which structural changes such as the formation of soil aggregations has on the suction/moisture content relationships may well give useful information on the nature of those changes.

Summary

Measurements of the suction and volume of soils as a function of moisture content and degree of disturbance are described. The work was carried out at the Road Research Laboratory as part of an investigation into the distribution of moisture in road and airfield foundations.

A classification of soils based on the shrinkage characteristics is used to present the results. Incompressible soils are exemplified by chalk and sand, fully compressible soils by a typical heavy clay, and partially compressible soils by a silty clay. It is shown that a range of moisture contents can be in equilibrium with a given suction and that this fact can be interpreted in terms of soil structure.

For compressible and partially compressible soils, it appears that a

unique relationship between suction and moisture content exists for each soil in the fully disturbed condition represented by the Atterberg limit tests.

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ISOTOPIC EQUILIBRIA BETWEEN PHOSPHATES IN SOIL AND THEIR SIGNIFICANCE IN THE ASSESSMENT OF FERTILITY BY TRACER METHODS

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Abstract

The isotopic exchange of phosphorus has been studied between solutions of orthophosphate and the following solid phases: anion-exchange resin charged with phosphate; dicalcium phosphate; rock phosphates; hydroxyapatite aged to varying extents; and natural soils.

The nature of exchange reactions in the soil is discussed. It is considered that all inorganic phosphate fractions in the soil undergo exchange with added phosphates, though at different rates.

Consideration is given to procedures proposed by earlier workers for the estimation of the phosphate status of the soil by tracer methods. In particular, the hypothesis that 'plant available' soil phosphate can be estimated by comparing the specific activity of phosphate added to the soil with that of phosphate absorbed by plants is examined. It is shown that the method is of limited application. It appears, however, that since 'plant-available' soil phosphate undergoes isotopic exchange more readily than 'unavailable' forms, it should be possible to estimate available soil phosphate by observing isotopic exchange between solutions and soil suspensions under controlled conditions. The appropriate procedure will vary between soil types and must be determined by *ad hoc* investigations.

The limitations which isotopic exchange and isotopic dilution effects impose on the estimation of fertilizer absorption by tracer methods are discussed.

Introduction

THE extent of isotopic exchange between different chemical forms of phosphate in the soil, and the consequence of this process in studies of the absorption of labelled fertilizers by plants, have been considered by a number of investigators. Spinks and Barber (1947) stated that such exchange did not affect the interpretation of their results. McAuliffe, Peech, and Bradfield (1949) noted that isotopic exchange would decrease the apparent utilization of labelled phosphate by plants. They were, however, unable to suggest the extent of this effect. Hendricks and Dean (1950) were of the opinion that exchange was so slight that it could not cause large errors in the estimation of fertilizer absorption under normal circumstances. Larsen (1952), however, claimed that isotopic exchange between mono- and di-calcium phosphates and soil

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phosphate was so great that the exchangeable-phosphate content of the soil could be determined by comparing the specific activity of labelled phosphate added to the soil with that of the phosphate subsequently absorbed by plants. Similar methods were used by Gunnarsson and Fredriksson (1953) to determine the 'plant-available phosphate' in soil. The values for 'plant-available phosphate' obtained by this method were similar to their estimates of the amount of phosphate which underwent exchange when aliquots of soil were shaken in solutions of labelled phosphate. Fried and Dean (1952) conducted experiments similar in type to those of Larsen. Their interpretation, however, contrasted with that of Larsen in two important respects; they considered isotopic dilution, as opposed to isotopic exchange, to be the important factor determining the specific activity of phosphate entering plants, and they concluded that a mathematical treatment similar to that of Larsen could be used to measure the amount of soil phosphate which was of the same degree of availability as the labelled phosphate which had been added to the soil.

These divergent interpretations indicate the desirability of examining the following questions in greater detail:

(i) The relationship between 'exchangeable' and 'available' phosphate. The use of isotopic exchange to estimate the amount of phosphate in soils which is available to plants implies that these fractions are identical, but this assumption is unsupported by critical data.

(ii) Whether the results of Larsen are in fact indicative of isotopic exchange or whether they should be attributed to a simple isotopic dilution effect as Fried and Dean imply.

(iii) Whether estimates of fertilizer absorption by the method of Spinks and Barber, and of Hendricks and Dean, can be regarded as valid in the light of the more recent investigations.

Some aspects of these subjects will be here examined.

In view of the varying interpretations which have been given to the words 'available' and 'availability', it is desirable to state the sense in which they are here used. It is assumed that if two sources of phosphate are present in a medium, the amounts of phosphate a plant absorbs from the two sources are proportional to the quantities of 'available' phosphate they contain. If, however, the two sources are to be adequately compared, it is necessary to consider not only the amount of available phosphate they provide, but also the total quantity of phosphate present in each source. Thus it is convenient to regard the 'availability' of each source as the ratio of available phosphate to total phosphate. Clearly, however, availability is a relative concept which cannot be expressed in absolute terms since the amount of phosphate any plant will absorb from a given source is determined by the interaction of many physiological and environmental factors.

In considering the interpretation of experiments in which labelled phosphate is used to provide information on the phosphate nutrition of plants, it is important to distinguish between the possible effects of two physical processes, namely 'isotopic dilution' and 'isotopic exchange'.

If an aliquot of a substance is introduced into a system in which diffusion is possible and which contains an isotopically distinguishable, but otherwise identical, form of the same substance, the ratio of the two isotopic forms in any sample withdrawn from the system after equilibration will indicate the relative amounts of the two forms in the entire system. This effect is known as 'isotopic dilution'. 'Isotopic exchange', on the other hand, implies the interchange of isotopically distinguishable, but otherwise identical atoms or groups between different phases or compounds. It is convenient to consider the nature of such reactions in a system containing the components (AX_m) and (BX_n), when (A) and (B) are two dissimilar atoms or groups, (X) is an atom or group common to both molecules, and (m) and (n) are the numbers of the group (X) in each molecule (Harris, 1951). If two distinguishable isotopes exist of an atom contained in the group (X), and if the two forms of the group are distinguished as (X^1) and (X^2), then the formulae of the two components of the system can be written as:

$$AX^1_{(m-g)}\,X^2_g \text{ and } BX^1_{(n-h)}\,X^2_h$$

when (g) and (h) are respectively the numbers of groups of the type (X^2) in each molecule. If the initial distribution of X^1 and X^2 between the two components in such a system is not an equilibrium one, isotopic exchange will cause equilibrium to be attained between the two components of the system according to the equation:

$$\frac{g}{m}=\frac{h}{n}. \qquad (1)$$

It follows from equation (1) that, if the common ion in one component of such a system was originally labelled with a radioactive ion, isotopic exchange will cause the specific activity of that component to be reduced and the other component to become labelled. Isotopic exchange reactions have been observed between molecules in solution and those on adjacent solid surfaces, and between molecules within crystalline solids (Imre, 1937). All exchange processes conform to the law of first order reversible reactions.

Since phosphate occurs in soil in a number of chemical combinations, the occurrence of a complex series of isotopic exchange reactions in the soil must be envisaged. The course of exchange may be expressed by the equation for a number of simultaneous, first order reactions:

$$A_0-x_t = A_1e^{-a_1t}+A_2e^{-a_2t}+A_3e^{-a_3t}+\ldots+A_ne^{-a_nt}, \qquad (2)$$

where (A_0) is the amount of P^{32} originally added; (x_t) the amount of the isotope which exchanged with phosphate in soil in time (t); (a_1), (a_2), (a_3), &c., are the respective velocity constants of the separate exchange reactions; (A_1), (A_2), (A_3), &c., are constants; and (n) is the number of separate exchange reactions which take place. The extent to which phosphate in organic complex in the soil undergoes exchange cannot be suggested. It is to be borne in mind that when phosphate is added to the soil in such quantity that the phosphate equilibrium of the soil is upset, phosphate will be rendered insoluble. The terms 'fixation'

and 'sorption' have both been used to describe this process. It is considered that 'sorption' is a more appropriate description since, as will be shown later, phosphate precipitated in this manner frequently remains readily exchangeable. Thus the process is in no way analogous to 'fixation' as that term is applied to nitrogen and other substances in soils. It is to be anticipated that the velocity constants of the separate exchange reactions will differ widely as also will those for the sorption processes.

Experimental Results

Before studying exchange reactions in such a complex system as soil, it was considered desirable to examine separately the exchange of surface-adsorbed phosphate and of precipitated phosphate with solutions of orthophosphate. Phosphate adsorbed on anion-exchange resin and basic calcium phosphates were used respectively for these purposes.

Exchange reactions with anion-exchange resins

Known amounts of Deacidite B, a synthetic anion-exchange resin of low basicity, which had been previously treated with a 0·01 molar phosphoric acid solution and then washed with water and air-dried, were suspended in 50 ml. of dilute phosphoric acid solution to which $H_3P^{32}O_4$ accompanied by a negligible concentration of carrier had been added. The weight of resin used in different experiments varied between 100 and 300 mg.; the strength of phosphoric acid varied between 0·007 and 0·04 N.; and the activity of the solution after the addition of P^{32} was approximately 0·01 μC. per ml. The experiments were carried out at room temperature, with the exception of two in which the temperature was maintained at 25° C.$\pm$0·1°. As the intention was to measure the distribution of P^{32} at equilibrium rather than to determine reaction velocities, small variations in temperature were considered to be unimportant. Samples of the supernatant liquid were withdrawn after different intervals and their activities were determined with a glass Geiger Mueller counting tube. When successive determinations showed no further change in the activity of the solutions, the P^{31} phosphate concentrations of the solutions were determined. In all experiments this state was reached in less than 48 hours. The quantity of phosphate originally adsorbed on the resin was determined in the solution obtained by extracting a portion of the resin with hydrochloric acid. This quantity added to the amount of P^{31} adsorbed from the solution gave the amount of P^{31} phosphate in the solid phase; the P^{32} in the solid phase was calculated from the decrease in activity of the solution. From these quantities the specific activity was calculated in terms of counts per minute per mg. P^{31} for both liquid and solid phases. The criterion of uniform distribution of the P^{32} throughout the P^{31} of the whole system is that the value of the ratio (specific activity in solid)/(specific activity in solution) approaches unity. The results obtained are given in Table 1. The estimates of error shown in the table have been computed from the combined errors of the analytical procedures used for the determination of P^{31} and P^{32}.

It is seen that the values for the ratio of the specific activities are sufficiently close to unity to justify the conclusion that exchange reactions

TABLE 1

Distribution of Radioactive Phosphate between Phosphate in Solution and Phosphate adsorbed on Deacidite B at Equilibrium

Wt. of Deacidite (g.)	*Initial concentration of solution*		*Temperature*	*Sp. act. in solution / Sp. act. in solid*	*S.E.*
	P^{32} *(μC/ml.)*	P^{31} *(moles/l.)*			
0·100	$2{\cdot}5 \times 10^{-4}$	0·01	Room	1·08	0·04
0·100	5×10^{-4}	0·01	,,	1·10	0·04
0·100	$2{\cdot}5 \times 10^{-4}$	0·02	,,	1·03	0·04
0·100	5×10^{-4}	0·02	,,	0·95	0·04
0·100	$2{\cdot}5 \times 10^{-4}$	0·04	,,	1·02	0·04
0·100	5×10^{-4}	0·04	,,	1·15	0·05
0·200	8×10^{-3}	0·0067	25° C.	1·02	0·04
0·200	16×10^{-3}	0·0075	25° C.	1·03	0·04
0·300	1×10^{-4}	0·01	Room	1·09	0·05
0·300	2×10^{-4}	0·01	,,	1·05	0·04
0·300	3×10^{-4}	0·01	,,	0·97	0·04

between adsorbed phosphate and phosphate ions in solution cause radioactive phosphate added to the solution to become uniformly distributed throughout all of the phosphate in the system.

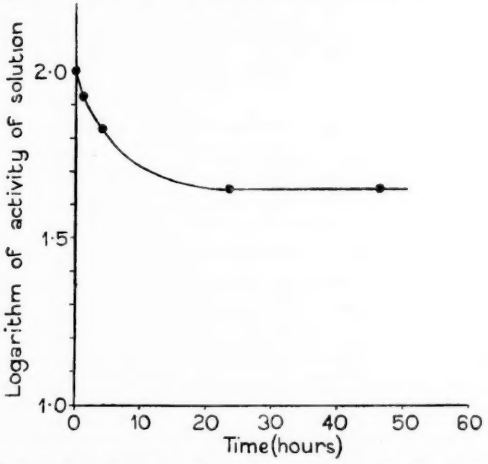

FIG. 1. Removal of radioactive phosphate from solution by Deacidite B. Weight of solid phase: 0·2 g. Volume of solution: 60 ml.

In one of these experiments samples were taken at sufficiently frequent intervals for the rate of removal of radioactive phosphate from the solution to be examined (Fig. 1). The shape of the curve may be interpreted as indicating the occurrence of a single rapid exchange reaction, which was substantially complete in less than 24 hours.

Exchange reactions with calcium phosphates

Similar exchange experiments to those described in the preceding section were carried out with dicalcium phosphate dihydrate, with basic calcium phosphates, and with naturally occurring rock phosphates. Since they have been reported in detail elsewhere (Rickson, 1953),

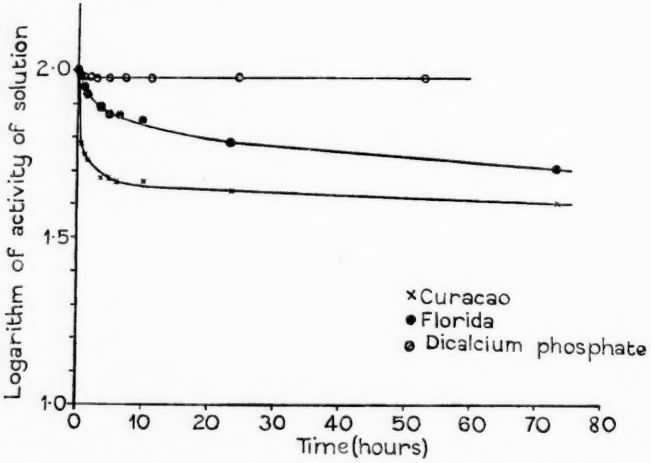

FIG. 2. Removal of radioactive phosphate from solution by Florida and Curacao rock phosphates, and by dicalcium phosphate. Weight of solid phase: 0·1 g. Volume of solution: 50 ml.

reference will be made only to the salient features. With dicalcium phosphate an initial rapid exchange took place during the first hour, after which time the system appeared to have reached equilibrium. With the rock phosphates, on the other hand, the exchange was still proceeding at a measurable rate after two days. Fig. 2 shows the removal of radioactive phosphate from solution as a function of time, for these solids. The curve for dicalcium phosphate is similar to that for Deacidite, in that an initial rapid exchange occurred, the activity of the solution thereafter remaining constant. The two rock phosphate samples behaved quite differently. In addition to a rapid initial exchange there was a slower prolonged exchange, the effect of which was clearly apparent after the initial reaction had virtually ceased. The same pattern of behaviour was exhibited by laboratory preparations of basic calcium phosphate approximating in composition to hydroxyapatite, but whereas approximately 0·2 per cent. of the phosphate in the rock exchanged in 24 hours, up to 25 per cent. of the phosphate in laboratory preparations exchanged in the same time (Rickson, loc. cit.).

The effects of crystal size on the rate of exchange of the laboratory preparations was examined in samples which had been aged by leaving them in contact with the solutions from which they had been precipitated for varying periods. In Fig. 3 the rates of removal of P^{32} from

solution are compared for samples which had been aged for 25 and 36 days. The samples which had been aged for the longer time, and in which local differences of surface energy were therefore smaller, showed the lower rate of exchange. It is considered that this indicates the importance of surface reactions in the exchange process. It may be

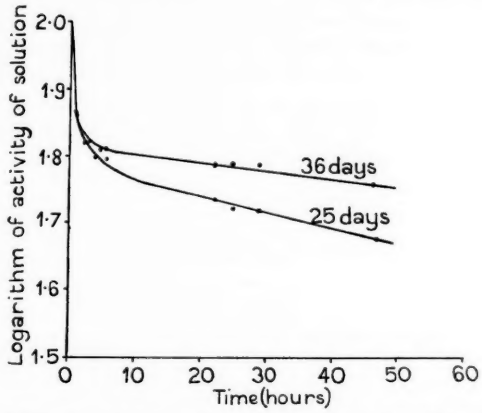

FIG. 3. Effect of ageing on removal of radioactive phosphate from solution by basic calcium phosphate. Weight of solid phase: 0·1 g. Volume of solution: 50 ml.

noted that samples which had been aged for only 9 days showed an anomalous behaviour; the extent of the initial rapid exchange was less than that for samples aged for 25 days, but the secondary exchange was more rapid than in the case of the older samples. If ageing resulted only in crystal growth, it would have been expected that the initial rapid exchange would be greater with recently precipitated material than with older samples. This anomaly is believed to be due to the fact that recently precipitated material of this type is, as Wallaeys (1952) has suggested, a non-stoichimetric solid solution, intermediate in composition between tri-calcium phosphate and hydroxyapatite, which becomes markedly more basic when left in the mother liquor for some days. Consequently the 9-day sample is not likely to be strictly comparable with the 25- and 36-day samples.

The slower absorption of P^{32}, which followed the initial rapid reaction in the experiments with rock phosphate and with basic dicalcium phosphate, could be explained by either or both of two mechanisms, namely the diffusion of radioactive ions into the interior of the crystalline solid or diffusion along microcracks. Imre (1937) has shown that diffusion into crystalline solids may result from recrystallization processes which occur when local differences of surface energy are found on crystalline surfaces. Hendricks and Hill (1950) have drawn attention to the importance of entrapped surfaces in the structure of apatite. The fact that no slow reaction followed the initial rapid exchange in the experiments with dicalcium phosphate is equally compatible with either interpretation. A nearly perfect crystal development in that substance would

cause little recrystallization to occur, and its existence in discrete crystals would prevent the effects of diffusion along microcracks.

Similar results to those here described for rock phosphates have been reported by Wiklander (1950), who found that isotopic exchange with iron phosphate consisted of a rapid surface reaction followed by a slow solid phase reaction.

Whilst this paper was in preparation the results of comparable adsorption experiments on rock phosphate and hydroxyapatite have appeared (Olsen, 1952). Olsen concluded that some of the P^{32} adsorbed in his studies was present on entrapped or inner surfaces, and could not be readily desorbed on suspending the solid in a phosphate solution free of P^{32}.

Exchange reactions in natural soils

It follows from the nature of exchange reactions that if an aliquot of soil is suspended in a solution containing $(x)P^{31}$ and $(y)P^{32}$ and isotopic exchange occurs, then,

$$\frac{y}{x+E_t}=\frac{y_t}{x_t} \tag{3}$$

when (x_t) and (y_t) are the amounts of P^{31} and P^{32} in the solution after time (t), and (E_t) is the quantity of soil phosphate which has undergone exchange. Hence,

$$E_t=\frac{x_t}{y_t}y-x. \tag{4}$$

If an attempt is made to estimate the exchange capacity of a natural soil by this procedure, difficulty arises from the fact that, if the concentration of labelled phosphate used is sufficiently large for accurate colorimetric measurements to be made, sorption will occur simultaneously with isotopic exchange. The effect of sorption on the validity of the calculated result will depend on the rapidity of exchange between the bathing solution and the phosphate sorbed during the experiment. Should exchange be so rapid that the sorbed phosphate remains virtually in equilibrium with the bathing solution the value of x_t/y_t will be unaffected by sorption and no error in the estimation of E_t will result. The rate of the process may, however, be affected, and the kinetics of exchange cannot therefore be studied. If, however, the phosphate sorbed during the experiment exchanges slowly or not at all with that in the bathing solution, its specific activity will exceed y_t/x_t at time t since exchange necessarily causes the specific activity of the solution to decrease during the experiment. x_t/y_t will therefore be increased by sorption and isotopic exchange will be overestimated by equation (4).

To overcome the complications due to sorption McAuliffe *et al.* (1947) allowed soils to equilibrate with water for 4 days and then added a quantity of 'carrier-free' P^{32} which it was considered would cause no significant change in the phosphate content of the solution. Exchange was measured by observing the disappearance of P^{32} from the solution. The validity of this procedure depends on the two assumptions that the P^{32} is added only after equilibrium has been attained, and that the carrier added with the P^{32} does not affect the phosphate balance of the

system. Small changes in the phosphate content of the solution, which would be difficult to detect by colorimetric methods, could introduce considerable errors especially in studies with soils of low phosphate status. It may be noted also that this procedure does not necessarily demonstrate the nature of the exchange process in the natural soil since, during equilibration with water, the balance between soil phosphate fractions may be altered.

An alternative procedure was adopted by Wiklander (1950). Samples of soil were shaken with labelled phosphate for 3 days; the bathing solution was then replaced by a solution of unlabelled phosphate of equal concentration, and the return of P^{32} to the solution was observed. The validity of this method for estimating the exchangeable phosphate content of the soil clearly depends on equilibrium between the initial labelled solution and *all forms* of exchangeable phosphate in the soil having been attained before the labelled solution was removed. That this condition was satisfied in Wiklander's investigation appears most improbable since equilibrium between the treated soil and the second solution was, as his results show, not reached in 4 days. A further criticism of the method used by Wiklander is that the amount of phosphate sorbed in the initial period was not considered, and his estimate of the exchangeable phosphate content of the soil included any phosphate sorbed during the initial treatment which was exchangeable.

The above considerations suggest that the procedures of McAuliffe *et al.* and Wiklander might give rise to errors which could not be readily detected. Thus it appeared preferable to attempt to employ the simpler method of shaking aliquots of soil with solutions containing known quantities of P^{31} and P^{32} and observe the changes in these quantities. If it could be proved that at the end of the experiment the phosphate which had been sorbed by the soil was in isotopic equilibrium with the bathing medium, it appeared that an unequivocal estimate of the exchangeable soil phosphate could be made.

The work was carried out at room temperature as the available shaking equipment could not be used in a thermostat. Thus variations in the rates of the slower exchange reactions were in all probability induced. This disadvantage was, however, considered to be small in a preliminary investigation.

Since the extent of the sorption of phosphate by soils will vary with the concentration of phosphate present in the solution in which it is suspended, the extent to which fixed phosphate remains in isotopic equilibrium with the solution can be investigated by shaking aliquots of soil in solutions containing varying concentrations of phosphate and comparing the values for (E_t) obtained by equation (4). If phosphate is sorbed in non-exchangeable form, the estimates will vary with the concentration of labelled phosphate applied. If, however, the sorbed phosphate remained exchangeable, the value for (E_t) will be constant. For the investigation of this question, a heavy loam soil (soil A) from Cumnor was used. The soil had a fairly high phosphate content resulting from liberal application of basic slag in previous years; 1·8 mg. P per 10 g. air-dry soil was soluble in 0·5 N. acetic acid and the pH was

7·8. Ten-gramme aliquots of this soil were shaken with 200 ml. of labelled phosphate solutions containing 2·5, 5, 10, and 20 mg. P. The amount of phosphate sorbed and the exchangeable soil phosphate (E_l) were calculated after intermittent shaking for 4 and 48 hours (Table 2).

TABLE 2

Soil A: Phosphate Fixation and Exchange as determined by Equilibration with Solutions differing in Phosphate Content

	Initial P^{31} *in solution (mg.)*	P^{31} *fixed (mg.)*	*S.E.*	*Exchangeable soil* P *(mg./10 g. soil)* (E_l)	*S.E.*
4-hour sample	2·5	0·93	0·01	0·61	0·01
	5·0	1·55	0·03	0·61	0·01
	10·0	2·29	0·02	0·86	0·09
	20·0	2·72	0·08	1·69	0·29
48-hour sample	2·5	1·40	0·02	1·49	0·10
	5·0	2·35	0·02	1·26	0·11
	10·0	3·30	0·05	1·59	0·31
	20·0	4·52	0·04	1·77	0·13

At the 4-hour sample the values for (E_l) were significantly lower in the 2·5 and 5 mg. P treatments than when 20 mg. P were applied. No significant difference, however, occurred between treatments in the 48-hour sample. It will be seen that on that occasion the soil treated with 20 mg. P had sorbed over three times as much phosphate as that treated with 2·5 mg. Moreover, the sorbed phosphate greatly exceeded the estimated value for exchangeable phosphate. Had the specific activity of the sorbed phosphate been significantly different from that of the solution at 48 hours, considerable differences would have been expected between the four estimates of (E_l). The results therefore provide strong evidence that after 48 hours a valid estimate of (E_l) could be made by equation (4). The higher values in the 20 mg. P treatment after 4 hours than in the 2·5 or 5 mg. P treatments suggest that equilibrium between sorbed phosphate and the solution had not then been attained. The fact that the values for (E_l) were identical in the 2·5 and 5 mg. treatments at 4 hours suggests, however, that errors due to sorption were insignificant when these quantities of phosphate were applied.

It was therefore considered justifiable to use this method for studying phosphate exchange in prolonged experiments. The high pH of soil A suggested that a considerable proportion of the soil phosphate might be in the form of calcium salts. Accordingly phosphate exchange was studied in this soil both in its natural state and after the replacement of exchangeable cations by ammonium according to the method of Piper (1944). Replicated 10-g. samples of the soil both untreated and treated in this manner were shaken with 200 ml. of a solution containing 5 mg. labelled phosphate and sampled after varying periods. Changes in the P^{31} and P^{32} content of the solutions are shown graphically in Fig. 4. The extent of phosphate sorption is indicated by the curves for P^{31}.

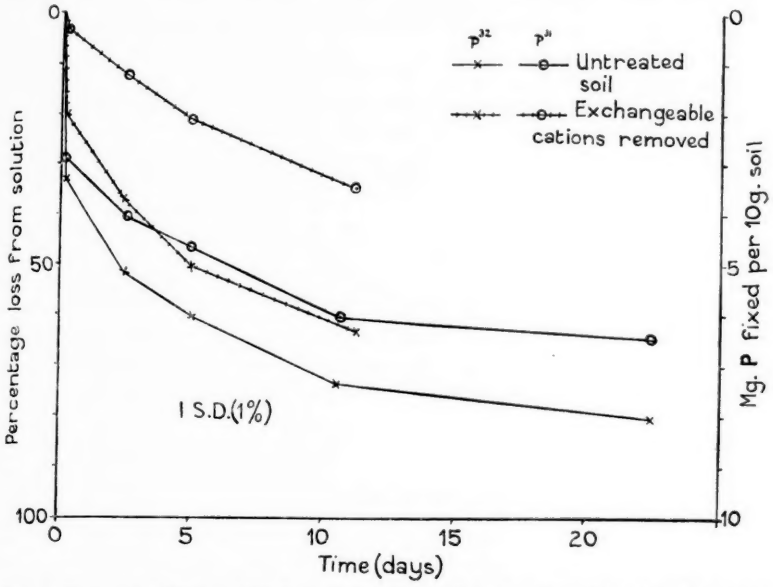

FIG. 4. Removal of P^{31} and P^{32} from solution by soil A, showing effect of exchangeable cations. The extent of phosphate fixation is indicated by the P^{32} curves. Weight of solid phase: 10 g. Volume of solution: 200 ml.

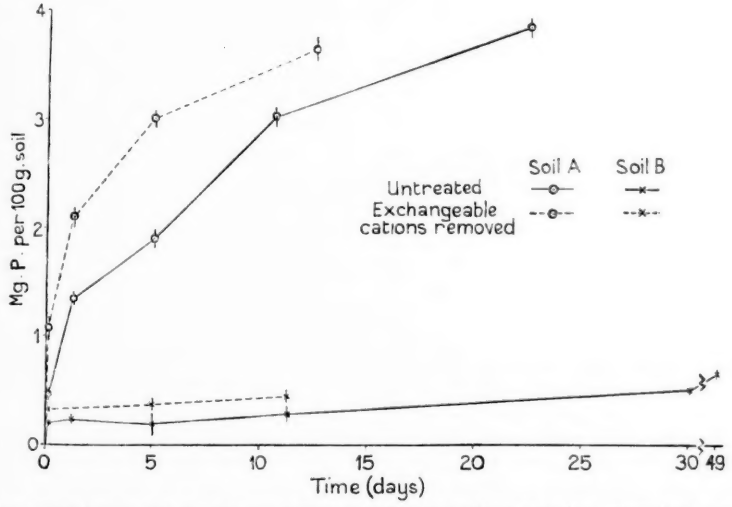

FIG. 5. Exchange of phosphorus between soil and bathing solution. Standard errors are shown.

The soil from which the exchangeable cations had been displaced showed considerably less sorption, particularly in the early stages of the

TABLE 3

Comparison of Estimates of Exchangeable and Acetic Acid Soluble Phosphate in Two Soils

	Exchangeable phosphate (mg. P per 10 g. soil)			*Acetic acid soluble phosphate (mg. P per 10 g. soil)*
	Day 2	*Day 24*	*Day 49*	
Soil A	1·35	3·89	..	1·8
Soil B	0·23	..	0·65	0·1

experiment. Thus it appears that in the untreated soil, a considerable fraction of phosphate was sorbed rapidly in association with calcium. The values for soil exchangeable phosphate (E_t) are shown in Fig. 5.

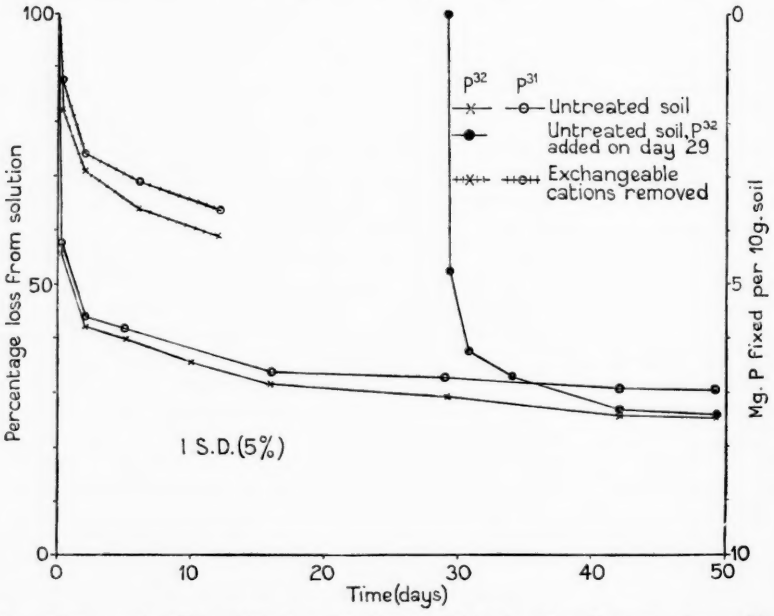

FIG. 6. Removal of P^{31} and P^{32} from solution by soil B, showing effect of exchangeable cations. The extent of phosphate fixation is indicated by the P^{31} curves. Weight of solid phase: 10 g. Volume of solution: 200 ml.

It is seen that exchange was markedly more rapid during the early stages of the experiment in the soil from which the exchangeable cations had been displaced. After 4 hours, 2·4 times more phosphate had undergone exchange in the soil from which exchangeable cations had been removed than in the untreated soil. With the passage of time the

ratio fell, the values being 1·6, 1·5, and 1·2 after 2, 5, and 12 days respectively. It thus appears that the rate of exchange of soil phosphates, rather than the amount of exchangeable soil phosphate, was increased by the displacement of exchangeable cations. Observations covering much longer periods would, however, be necessary to prove whether the total amount of exchangeable phosphate was affected. It is of interest that the exchangeable phosphate content of the soil was over twice the acetic acid soluble phosphate value (Table 3).

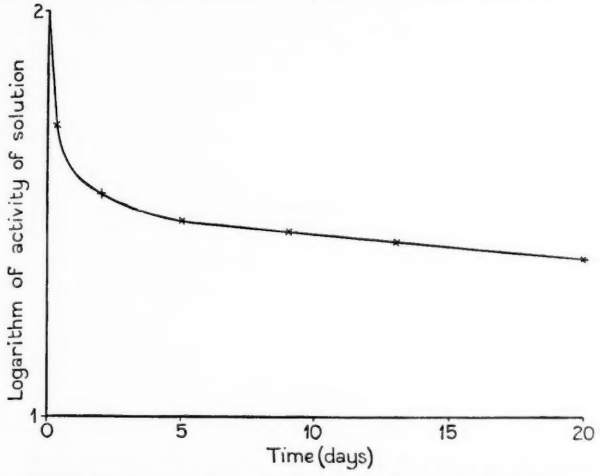

FIG. 7. Removal of P^{32} from solution by soil B. The soil was equilibrated with unlabelled phosphate for 29 days before addition of P^{32}.

In subsequent experiments a sandy top soil from Bagley (soil B) was employed. The acetic acid soluble phosphate in the soil was less than 0·1 mg./10 g. and the pH was 4·4. Ten-gramme aliquots of this soil were treated with labelled phosphate in the manner already described, but in addition some replicates were shaken with unlabelled phosphate for 29 days, after which period $KH_2P^{32}O_4$ was added. Spectrographic analyses of the tracer solution showed that the level of carrier was so low that the total phosphate content of the solution was not affected significantly. After a subsequent period of 10 days, the percentage of tracer lost from the solution was the same in the replicates which had been treated with P^{32} at the commencement of the experiment as in those treated on the 29th day (Fig. 6). Since the sorption of phosphate was virtually complete after 29 days, this result justified the conclusion that the phosphate sorbed during the experimental treatment remained in an exchangeable form. It was legitimate, therefore, to calculate exchangeable phosphate by equation (4). The values both for the untreated soil and for the soil from which exchangeable cations had been displaced by ammonium are shown in Fig. 5. The exchangeable phosphate in soil B, like that in soil A, greatly exceeded the acetic acid soluble phosphate (Table 3).

The exchangeable phosphate content of soil B was considerably smaller than that of soil A, and in consequence experimental errors were proportionately greater. Despite the fact that a more sensitive procedure would clearly be necessary for a detailed study of the exchange capacity of soil B, it resembled soil A in certain respects: exchange was apparently incomplete at the conclusion of the experiment and initially exchange tended to be more rapid in the soil from which exchangeable cations had been displaced. In the untreated soil the value for exchangeable phosphate decreased between day 2 and day 5. This effect was not statistically significant; it may, however, indicate that some days were necessary for the phosphate sorbed at the commencement of the experiment to reach equilibrium with the solution, the specific activity of which was decreasing rapidly at that time. Such an effect would have been much less apparent with soil A on account of its higher phosphate status.

As the sorption of phosphate was virtually complete when P^{32} was added on the 29th day to the solution in which the soil was suspended, the kinetics of the subsequent exchange may be examined. Fig. 7 shows that a rapid reaction was followed by a slower secondary exchange. The form of the curve resembles those obtained with rock phosphate and basic calcium phosphate (Figs. 2 and 3).

Discussion

Nature of isotopic exchange reactions in soils

The observations of exchange between soil suspensions and the bathing medium here reported demonstrate that after a considerable period—49 days in one experiment—isotopic equilibrium had not been attained. The experimental procedure precluded the study of the kinetics of the reaction except in one experiment (Fig. 7), but it was apparent that velocity of exchange decreased with time. The results therefore support the conclusion of McAuliffe *et al.* (1947) and Wiklander (1950) that a rapid exchange reaction is followed by a slower process. It may be assumed that a significant part of the initial rapid exchange is due to the reaction between the solution and phosphate adsorbed on surfaces. The exchange of phosphate between anionic exchange resins and solutions in which they are suspended is considered to be a similar process. It has been shown that the exchange process in such systems rapidly attains equilibrium, and the kinetics of the process suggest the occurrence of a single exchange reaction. The occurrence of two or more simultaneous reactions of comparable velocity is not, however, excluded by the present data. Wiklander reports the attainment of a correspondingly rapid equilibrium with another exchange resin, but information on the kinetics of the reaction are not given. In contrast with this rapid exchange is the reaction between calcium and iron phosphates and the bathing medium; Rickson (1953) and Wiklander (loc. cit.) have shown that these substances exhibit a rapid initial exchange followed by a slower process.

The complexity of the exchange reaction which occurs in different phosphate fractions in soil is clearly apparent; the present limited data support the conclusion that *all inorganic phosphate fractions in soil must be regarded as undergoing exchange although at very different rates.* Depending on the nature of the soils, on the exchangeable cations present, and on the surface development of the precipitated phosphates present, the rate of the process may vary widely. For example, the replacement of replaceable cations by ammonium (Fig. 5) or by potassium (Wiklander, loc. cit.) causes a marked acceleration. Temperature may also be expected to affect the rates of the slower processes which depend on the dissociation constants of the solid fractions. On this question Wiklander has presented data.

The limitations of the methods for investigating exchange used both in the present and in previous work have been considered in earlier sections. They indicate the undesirability of postulating any detailed interpretation until more conclusive evidence is available. It is, however, apparent that the 'exchangeable' and 'plant available' phosphate in the soil cannot be regarded as equivalent. The former may be expected to exceed the latter to an extent which will vary between soils, depending on the amount of sparingly available or unavailable phosphate present. It is of interest that in the present experiments the acetic acid soluble phosphate in the soils studied was but a small fraction of the exchangeable phosphate (Table 3).

The use of radioactive phosphorus to estimate the phosphate status of soils

Larsen (1952), Fried and Dean (1952), and Gunnarsson and Fredriksson (1953) attempted to assess the phosphate status of soils by comparing the specific activity of the phosphate absorbed by plants with that of fertilizer which has been added to the soil. Despite difference in mathematical treatment and the interpretation of results, the methods of the three groups of investigators were essentially the same; thus for convenience in discussion, only the nomenclature of Fried and Dean will here be used. These workers assumed that the absorption of phosphate from a soil treated with labelled phosphate could be regarded as a simple isotopic dilution so that:

$$\frac{(A)\text{ soil}}{(B)\text{ soil}} = \frac{(A)\text{ plant}}{(B)\text{ plant}} \qquad (5)$$

when (A) and (B) are the available soil phosphate and fertilizer phosphate respectively.

From this equation the following expression was derived for the estimation of the available phosphate content of the soil:

$$A = \frac{B(1-y)}{y} \qquad (6)$$

when y represented the proportion of the nutrient in the plant which was obtained from the fertilizer.

y was calculated as follows:

$$y = \frac{(B) \text{ plant}}{(A) \text{ plant} + (B) \text{ plant}} \tag{7}$$

(y) therefore equals the ratio of the specific activity of the phosphate recovered from the plant to that of the fertilizer phosphate. Equation (6) can therefore be written more simply as:

$$A = B\left(\frac{S_f}{S_p} - 1\right), \tag{8}$$

when S_f and S_p represent the specific activities of the fertilizer phosphate and of the phosphate absorbed by the plant respectively. The significance of the value of (A) obtained by equations (6) or (8) has been variously interpreted. Fried and Dean described it as the available soil phosphate determined in terms of a 'standard', namely the form of fertilizer applied. They implied that this method is of universal application to nutrient absorption from the soil. Larsen and Gunnarsson and Fredriksson respectively defined (A) as 'exchangeable' and 'available' soil phosphate. The latter workers recognized, however, that the method was applicable only if equilibration had occurred between the fertilizer and soil phosphate in the soil. It is apparent from the nature of isotopic exchange in the soil that Larsen was in error in believing that 'exchangeable' soil phosphate could be measured by this procedure. It remains for consideration whether valid estimates of 'available' soil phosphate can be expected.

As Fried and Dean recognized, their procedure depended on the assumption that equation (5) was applicable, that is to say that the concept of simple isotopic dilution within the plant was valid. The equilibration between two or more isotopes which obtains in any isotopic dilution effect is due to the rates of diffusion or reaction of the different isotopes being identical within the limits of experimental measurement. Applying this principle to the present case, equation (5) will be strictly applicable only if the 'availability' of the fertilizer and of the soil phosphate are identical. If these requirements are not fulfilled, no simple relationship will exist between

$$\frac{(A) \text{ soil}}{(B) \text{ soil}} \text{ and } \frac{(A) \text{ plant}}{(B) \text{ plant}}.$$

The relationship will be expressed by the equation:

$$\frac{(A) \text{ soil}}{(B) \text{ soil}} = X\frac{(A) \text{ plant}}{(B) \text{ plant}}. \tag{9}$$

(X) will depend both on the relative availability of (A) and (B) and on their concentrations in the soil. If, for example, (B) is a sparingly soluble phosphate and (A) is by comparison highly soluble, and if (as may be assumed for this discussion) availability is related to solubility, then (B) is less available than (A), and (X) will be less than 1. The magnitude of (X) will, however, vary depending on the concentration of both (A) and

(B), since as the concentration of ($A+B$) is increased, the amount of the sparingly soluble (B) which dissociates will be reduced and its availability will be comparably depressed. Hence, if equation (9) and not equation (5) is applicable, varying values of (A) will be obtained by the use of equation (6), depending on the amount of fertilizer phosphate added.

Despite the fact that the above discussion is an obvious simplification, it provides some basis for considering the results which may be expected if equations (6) or (8) are applied to experimental results.

Three types of soil/fertilizer system may be considered:

Type I. If the soil has a high content of calcium phosphate and if the pH is not low, it is reasonable to infer that the soil contains a considerable phosphate fraction of comparable availability to a phosphate fertilizer such as mono- or di-calcium phosphate. Hence, if labelled superphosphate or other 'soluble' phosphate is added to the soil, the situation will approximate to that necessary for equation (5) to be valid. Thus, reasonably consistent values of (A) may be expected with a soil of this type when varying quantities of labelled fertilizer are employed.

Type II. If a soil similar to that in Type I is treated with 'insoluble' phosphate in labelled form, e.g. tricalcium phosphate, the fertilizer will be less available than a significant fraction of the soil phosphate. Equation (9) is applicable to this case, (X) being less than 1. Higher values of (A) will therefore be obtained by applying equations (6) or (8) and the magnitude of (A) will increase as the quantity of labelled fertilizer added to the soil is increased.

Type III. If soluble phosphates are added to soils in which reversion to unavailable forms occurs to a marked extent, a fraction of the fertilizer may be rendered less available than such phosphate as was available in the untreated soil. Under such circumstances, the possibility of isotopic exchange between the fertilizer and less available soil phosphates cannot be excluded. Both these processes will reduce the absorption of P^{32} by plants. Thus, equation (9) and not equation (5) will be applicable, and the values of (A) will be affected in the same general manner as in Type II. The effect of the amount of fertilizer employed on the values of (A) will, however, be more complex; variation will occur not only for the reasons outlined in the discussion of the magnitude of (X) in equation (9), but also because the extent of the processes of exchange and sorption will be influenced by the degree to which the equilibrium between the different phosphate fractions in the soil is upset.

The results of Larsen, of Gunnarsson and Fredriksson, and of Fried and Dean appear to accord with these expectations. Larsen obtained constant values for (A) when 'soluble' phosphates were employed in soils of reasonable phosphate status; the experience of Gunnarsson and Fredriksson was comparable. Two of the three soils which Fried and Dean treated with varying concentrations of superphosphate were of moderate or high phosphate status and they again gave consistent values of (A). Within the limits of experimental error, all these experiments appear to have fulfilled the requirements of Type I. Larsen, however, obtained much higher values by equation (8) when tricalcium phosphate

was substituted for soluble phosphate and the values increased with increasing dressings of fertilizer: this experiment, therefore, accords with expectations for Type II. Despite the fact that Fried and Dean state that their experiments show 'but little effect of a 32-fold change in rate of application on the calculated A values', when they applied super-

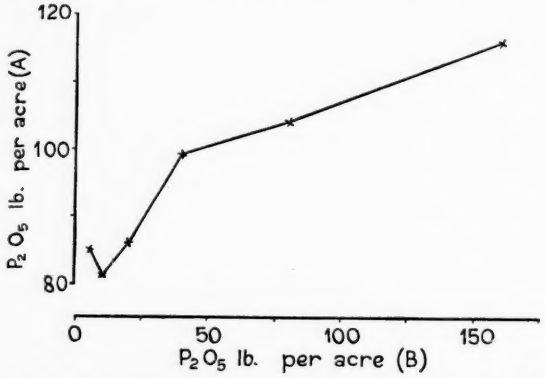

FIG. 8. Relationship between estimated 'available soil phosphorus' (*A*) and amount of labelled superphosphate added to the soil (*B*) in a soil of low phosphate status. Data of Fried and Dean (1952).

phosphate to a soil of 'very low available phosphorus' a considerable increase in (*A*) was induced by increasing levels of fertilizer. The relevant data are reproduced in Fig. 8. The authors made no explanation of this discrepant result which was in sharp contrast to their findings with soils of higher phosphate status. It is here suggested that the data shown in Fig. 8 are an example of Type III. It appears, therefore, that the interpretation of equations (6) and (8) advanced in the preceding paragraph agrees with the available data. It must, however, be stressed that the published results are inadequate for critical analyses. In particular, the fact that the method employed by Fried and Dean did not ensure that fertilizer and soil phosphate were equally distributed throughout the zone of root growth opened the way to large errors which cannot be assessed.

The foregoing discussion points to the conclusion that the methods of assessing the phosphate status of the soil which depend on comparison of the specific activity of fertilizer phosphate with that of phosphate absorbed by the plants are subject to considerable limitations. Under favourable conditions (i.e. Type I) a measure of the soil phosphate which is of similar availability to the added fertilizer is obtained. In other circumstances (i.e. Type II and Type III) the calculated values of (*A*) represent no definable fraction of the soil phosphate. Accordingly, the method does not provide a reliable measure of the phosphate status of soils in which a low percentage of the inorganic phosphate is readily available. This is a serious limitation since it is for such determinations that new and precise methods are of particular importance. Moreover,

it would seem impossible to attach any absolute meaning to 'availability' measured in terms of superphosphate as a 'standard' when comparing soils in which variable and unknown amounts of superphosphate may be rendered unavailable. Finally, it is pertinent to suggest that evidence is at present lacking to show how such methods can yield any greater information of agricultural value than the observation of the increase in the phosphate absorption of plants induced by the application of unlabelled fertilizer to different soils.

In addition to the investigations referred to above, Gunnarsson and Fredriksson attempted to assess available soil phosphate by observing the extent of isotopic exchange between aliquots of soil and phosphate solutions under standardized conditions. The results they obtained for four soils appeared markedly more reasonable than those derived by lactic acid extraction. It is apparent from the data on phosphate exchange discussed in an earlier section that the proportion of the exchangeable soil phosphate which undergoes exchange during a given period will vary greatly between soils, and that many factors will affect the rate of this process. Estimates by the method of Gunnarsson and Fredriksson are for these reasons necessarily empirical; with different soil types, different conditions of equilibration may be necessary to obtain exchange values which bear some relation to 'available' phosphate. However, since it appears reasonable to assume that the more readily exchangeable phosphates in the soil are those which are more available to plants, the method appears to deserve serious examination. It is to be noted that in contrast to the procedures depending on plant analysis, the exchange method is much simpler and more susceptible to routine laboratory organization. None the less, it is clear that the method cannot be regarded as more than an interesting possibility until considerably more information is available.

The effect of isotopic exchange in the study of fertilizer uptake

Hitherto the majority of investigators who have used P^{32} in fertilizer investigations have sought to determine the extent to which fertilizers are absorbed by plants. If the isotopic exchange of phosphorus occurs between the fertilizer and phosphate compounds in the soil, the specific activity of the fertilizer phosphate will be reduced. The effect of this on the estimation of the absorption of phosphate from the fertilizer will now be considered:

Let (F_s) be the weight of phosphate in the labelled fertilizer added to the soil;
(A_s) be the activity of tracer present in (F_s) fertilizer;
(F_p) be the weight of phosphate from labelled fertilizer which is absorbed by the plant;
(A_p) be the activity of tracer absorbed by the plant;
(E_s) be the weight of soil phosphate which undergoes exchange with the fertilizer phosphate in the soil during an experiment;
(E_p) be the weight of fraction of (E_s) which is absorbed by the plant.

In the absence of isotopic exchange the following relationship will apply:

$$A_p = \frac{F_p}{F_s} A_s. \tag{10}$$

Since (F_s), (A_s), and (A_p) can be determined experimentally, (F_p) can be derived. If, however, isotopic equilibrium has been attained in the soil between (E_s) and (F_s) the appropriate equation is

$$A_p = \frac{F_p+E_p}{F_s+E_s} A_s. \tag{11}$$

If the validity of the measurement of fertilizer absorption is not affected by exchange, it follows that the values of (A_p) derived by equations (10) and (11) will be identical.

$$\text{i.e.} \quad \frac{F_p}{F_s} = \frac{F_p+E_p}{F_s+E_s}, \qquad \text{i.e.} \quad F_pE_s = E_pF_s \quad \text{or} \quad \frac{F_p}{F_s} = \frac{E_p}{E_s}. \tag{12}$$

That is to say, the availability to the plant of the exchangeable soil phosphate and the fertilizer phosphate must be identical. If the exchangeable soil phosphate is less available than fertilizer phosphate, fertilizer uptake will be underestimated; if it is more available, fertilizer uptake will be overestimated. In the majority of experiments it is to be expected that the exchangeable soil phosphate will be less available than fertilizer phosphate; thus an underestimation of fertilizer uptake should be the more common error.

It is thus apparent that isotopic exchange must be taken into account in interpreting the results in such investigations. Since no measurements of isotopic exchange in soils of normal water content are available, the extent of this effect cannot be assessed. Clearly, however, a complex situation must be expected. (F_p) must be expected to exchange most rapidly with readily available soil phosphates and less rapidly with less available forms. During the course of an investigation, the pattern of the effect may therefore vary. It is important to note that this situation does not imply any difference in behaviour between the two isotopes of phosphorus present in the labelled fertilizer. Both isotopes will exchange at the same rate but the exchange of P^{32} in the fertilizer for P^{31} in the soil will alone lead to detectable effects.

The results of Larsen, Gunnarsson and Fredriksson, and Fried and Dean already referred to suggest, however, that even if little isotopic exchange has occurred, the significance of results may not be as simple as is apparent at first sight. If the values of (A) obtained by equations (6) and (8) indicate the quantity of soil phosphate which is of the same availability to the plant as the added fertilizer, experiments with labelled fertilizers must be regarded as of no greater value for the estimation of the absorption of fertilizers by plants than for the assessment of the phosphate status of the soil. It is hard to see how knowledge of the response of crops to fertilizers will in normal experiments be advanced more by tracer studies of absorption than by the observation of the increase in the phosphate content of plants induced by the application

of fertilizer, which can be determined by normal chemical methods. In fact, the examination of the total phosphate content of plants may be a better means for practical purposes as it will reflect also increased soil absorption which may result from increased root development. The use of tracer methods would seem more appropriate for special purposes such as the determination of the soil zones from which absorption is most rapid, in studies of fertilizer placement and in the examination of the 'reversion' of phosphate fertilizers.

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THE RELEASE OF SILICA FROM SOILS BY THE ORTHOPHOSPHATE ANION*

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THE significance of the role of colloidal solutions of silicic acid in soil-forming processes, particularly with respect to the Mediterranean Terra Rossa soils, has been expounded by Reifenberg (1927, 1929, 1947).

Preliminary studies in this laboratory indicated that sodium salts of chloride, nitrate, sulphate, borate, hypobromite, and acetate anions do not effect a significant release of silica from soils or from kaolinite, whereas the phosphate anion does. The presence of orthophosphates in solution in contact with soils or clay minerals resulted in appreciable amounts of silica entering the solution phase, while at the same time (except for alkaline reactions) some phosphate was being attached to the solid phase—in other words, a displacement of silica accompanied phosphate fixation. In view of its importance in soil fertility as well as in weathering and soil-forming processes a study of this phenomenon was undertaken. This paper deals with one phase of that study, namely, the influence of certain factors affecting the quantity of silica displaced. Discussion of the mechanism involved is left for a forthcoming paper. It may be mentioned that later studies by the authors have revealed that a number of other anions, including certain products of biological activity in soil, also exhibit this property of releasing silica from the solid phase of soils and clay minerals.

Methods

Samples of air-dry soil (< 2 mm. diameter) in stoppered 500-ml. Pyrex flasks were shaken with sodium-phosphate solution and allowed to stand at room temperature for 72 hours with occasional shaking. The amount of soil used was equivalent to 100 g. on an oven-dry basis, and the sodium-phosphate solution was such as to give a total solution volume of 250 ml. and a concentration of one-third molar (1 N) with respect to phosphate. The phosphate solutions were prepared by mixing M/3 solution of NaH_2PO_4 and of Na_2HPO_4 to obtain the desired pH. The solution also exerted some buffer effect. Any variations, according to the factor being investigated, in amount of soil, volume and concentration of solution, and time of standing, are indicated in the text.

The pH of the clear filtrate was electrometrically determined by the glass electrode. The silica content was gravimetrically determined by the acid-dehydration method followed by hydrofluorization in the presence of sulphuric acid (Kolthoff and Sandell, 1943). The tedious classical gravimetric method was followed since preliminary trials had shown that the colorimetric method of silica determination as ammonium silicomolybdate (Snell and Snell, 1936) was unreliable for these experiments. The removal of interfering phosphate ions prior to the

* This paper includes part of a Ph.D. thesis by the junior author.

colorimetric determination had failed to give results of sufficient accuracy. Analytical results are given on the basis of 100 g. of oven-dry soil.

The Pyrex flasks used were previously thoroughly cleaned by treating with hot sodium hydroxide as well as with hot concentrated hydrochloric acid. The possibility of silica contamination due to the flask was checked by a blank trial with sodium-phosphate solution. Also, parallel trials involving soil as well as the phosphate solution were run in flasks lined with a thick inside coating of high-grade paraffin; but the results did not differ from those in unlined flasks. These flasks were therefore considered suitable for the experiments.

The Israeli soils used in these studies are described by Reifenberg (1947). The samples of clay minerals and of the chernozem profile were kindly provided by the Bureau of Plant Industry, &c., of the U.S. Department of Agriculture.

Results

The release of silica by phosphate

(*a*) *From different soils.* The release of silica from different soils by neutral phosphate solution is shown in Table 1. The treatments were carried out at room temperature for 72 hours. The phosphate effected a significant release in greatly differing soil material, over and above the amount of water-soluble silica. The coarser-textured soils showed less silica release by phosphate than the finer-textured soils.

TABLE 1

Release of Silica from Different Soils by Normal (M/3) Sodium-phosphate Solution of pH 7·00, and by Distilled Water

Solution:soil ratio, 2½:1. Time, 72 hours.

		Phosphate extract		*Water extract*
Soil	*Location*	*pH of resulting filtrate*	*m.mol.* SiO_2 *released per 100 g.*	*m.mol.* SiO_2 *dissolved per 100 g.*
Terra Rossa clay loam	Lower Galilee Hills	6·91	0·49	0·052
Alluvial clay loam	Lower Galilee, Natufa Valley	6·85	0·48	0·036
Basaltic clay loam	Lower Galilee Hills	6·81	0·39	0·057
Black Kabara clay loam	Sharon Plain	8·51	0·46	0·066
Basaltic alluvial Lisan Marl clay loam	Upper Jordan Valley	7·59	0·38	0·064
Nazzaz hardpan, sandy loam	Sharon Plain	6·98	0·30	..
Negeb sand	Beersheba area	7·09	0·20	0·032
Greensboro loam A_2 hor. (Podzol)	Eastern Canada	6·97	0·24	0·015
Kaolin, N.F. washed powder	J. T. Baker Chemical Co.	6·98	0·52	0·105

(*b*) *As a soil-depth function.* Like other soil properties the displaceable silica may show its own vertical distribution pattern in natural soil

profiles. The soil used for this exploratory purpose was a Barnes loam (from Spink County, South Dakota, U.S.A.), a chernozem soil developed on highly calcareous glacial till. In this series 10-g. samples of soil were shaken with 500 ml. of one-third molar sodium-phosphate solution of pH 7·00 and kept at 20° C. for 72 hours with occasional shaking. The amount of silica entering the clear solution is given in Table 2 as millimoles SiO_2 per 100 g. of oven-dry soil.

TABLE 2

Silica Release from a Chernozem Soil Profile by Neutral Normal (M/3) Sodium-phosphate Solution

Solution:soil ratio, 50:1. Time, 72 hours.

	Soil properties		*Phosphate extract*	
Depth (in.)	*Hygroscopic moisture (%)*	*pH**	*pH of filtrate*	SiO_2 *released (m.mol./100 g.)*
0–7	2·9	6·99	7·00	0·12
7–14	3·7	7·15	7·00	0·69
14–18	3·5	7·80	7·00	0·46
18–42	2·2	8·35	7·08	1·13

* 5:1 water:soil suspension.

The A_1 horizon showed a relatively very low release of silica; while the C_1 horizon, little affected by the biosphere, contained more phosphate-displaceable silica than the horizons above it.

(*c*) *From different clay minerals.* Four different known clay minerals were compared:

(1) Kaolinite—from Hawthorne, Florida.
(2) Halloysite ($2H_2O$)—type Indianaite (collected by E. Callahan).
(3) Illite—from Dr. R. E. Grim's collection.
(4) Montmorillonite—Wyoming bentonite (Volclay).

Portions of each equivalent to 5 g. on an oven-dry basis were suspended in 250 ml. of neutral, one-third molar (1 N) with respect to PO_4, solutions of sodium phosphate and of ammonium phosphate in parallel series, and were allowed to stand for 24 hours at 18° C. Results of analyses of the clear solution are given in Table 3. With this high solution:soil ratio (50:1) the pH of the solution remained the same as its initial value.

The amount of silica released in 24 hours was in the following order:

For the Na^+ series: montmorillonite > halloysite > illite > kaolinite.
For the NH_4^+ series: montmorillonite = halloysite > kaolinite ⩾ illite.

The average of both Na^+ and NH_4^+ phosphate series shows that illite and kaolinite released close to 1·2 millimoles SiO_2 per 100 g., while halloysite released twice that amount and montmorillonite three times that amount.

TABLE 3

*Silica Release from Different Clay Minerals by Normal (M/3) Solutions of Sodium and Ammonium Phosphate at pH 7·00**

Solution:soil ratio, 50:1. Time, 24 hours.

Clay mineral	*Hygroscopic moisture* (%)	SiO_2 *released by* PO_4 *soln. of*		
		Na (*m.mol./100 g.*)	NH_4 (*m.mol./100 g.*)	*Average* (*m.mol./100 g.*)
Kaolinite	0·9	1·59	0·83	1·21
Halloysite	2·9	2·66	2·17	2·42
Illite	3·0	1·96	0·67	1·32
Montmorillonite	8·4	5·00	2·25	3·62

Factors affecting the reaction

(*a*) *Accompanying cation.* It is obvious from Table 3 that the cation present is a factor affecting the release of silica. For all four minerals the silica release was greater in the Na^+ system than in the NH_4^+ system. The release by the Na^+ phosphate was at least double (except for the halloysite) that by the NH_4^+ salt at the same pH and concentration.

(*b*) H_3O^+*-ion concentration.* The data presented in Tables 1 to 3 indicate a release of silica from different soils and clay minerals at a neutral reaction and at ordinary temperature. Previous reports (Toth, 1937; Low and Black, 1948, 1950) on silica release by phosphate fixation concern rather highly acid conditions not found in many natural soils. Toth found that at pH 3·3 to 5·8 phosphate 'adsorption' by soil colloids displaced silica. He noted that the combined effect of increasing phosphate concentration and decreasing pH was an increase in the release of silica, but the specific effect of either factor alone was not ascertained. Recently Low and Black report a silica release with phosphate fixation by kaolinite. They worked at a buffered pH of 4·5 (1948) and of 4·5 to 5·1 (1950), and at 60° C. and 45° C. respectively.

The effect of varying pH upon silica release was studied by using different proportions of the primary and secondary phosphate salts (also the tertiary salt or some phosphoric acid in the more extreme cases) so as to obtain the given pH levels at the same PO_4 concentrations. Two concentrations of phosphate were used, 1 N (M/3) and 0·1 N (M/30). Three soils of clay loam texture, from the Lower Galilee Hills Region of Israel, were used, namely (1) basaltic soil, (2) Terra Rossa soil, and (3) Natufa Valley alluvium. The treatments were carried out at room temperature for 72 hours. The results are presented in Table 4 and in Figs. 1 to 3, the silica release being plotted against the final pH of the clear solution.

The data for the three soils agreed rather closely. The release of silica was highly sensitive to pH. The reaction was least at approximately pH 7·5, increasing at pH values above and below this. Below pH 7·5

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the increasing release of silica from the solid phase was accompanied by a fixation of phosphate. The data regarding this part of the curve were most complete for the basaltic soil treated with the 1 N phosphate (Fig. 1). An analysis of these data shows, for filtrate-pH values from 4·5 to 7·4, a highly significant inverse rectilinear relationship between the logarithm of silica release and the pH. The correlation coefficient, r_{xy}, is −0·9993.* The equation of this regression, by the method of least squares, is:

$$\log_{10} \text{millimoles } SiO_2 = 1{\cdot}755 - (0{\cdot}319 \times \text{pH}).$$

i.e.

$$\text{moles } SiO_2 = 0{\cdot}0569[H_3O^+]^{0{\cdot}319}.$$

TABLE 4

Release of Silica from Three Lower Galilee Soils by Sodium-phosphate Solutions of Different pH Values and Concentrations

Solution:soil ratio, 2½:1. Time, 72 hours.

PO_4 *soln.*			*Millimoles* SiO_2 *released per 100 g.*	PO_4 *soln.*			*Millimoles* SiO_2 *released per 100 g.*
Conc.	*Initial pH*	*Filtrate pH*		*Conc.*	*Initial pH*	*Filtrate pH*	
			Basaltic soil				
N/1	3·00	4·51	2·08	N/10	3·00	5·82	0·66
	5·00	4·88	1·63		..	..	..
	6·00	5·65	0·85		6·00	6·34	0·32
	7·00	6·81	0·39		7·00	6·88	0·25
	8·00	7·39	0·25		8·00	7·32	0·02
	10·00	7·90	0·33		..	..	..
	11·70	11·16	1·06		11·60	8·82	0·16
			Terra Rossa soil				
N/1	4·00	5·08	1·64	N/10	3·00	6·66	0·45
	6·00	5·85	0·94		6·00	6·90	0·32
	7·00	6·91	0·49		7·00	7·51	0·12
	8·00	7·23	0·30		8·00	7·60	0·07
			Alluvium (Natufa Valley)				
N/1	4·00	5·06	1·68	N/10	3·00	6·68	0·46
	6·00	5·72	0·89		6·00	6·88	0·24
	7·00	6·85	0·48		7·00	7·58	0·13
	8·00	7·33	0·21		8·00	7·70	0·14

(*c*) *Phosphate concentration.* In order to observe the effect of varying the phosphate concentration of the solution, 100 g. of basaltic soil were treated with 250 ml. of pH 6·00 sodium-phosphate solutions of different concentrations for 72 hours at room temperature. The results are given in Table 5. The amount of released silica increased with increasing phosphate concentration. However, due to the different degrees of buffering, the final pH values varied sufficiently to prevent a true comparison of the results. In Table 6 the effect of varying phosphate concentration upon silica release is compared at the same final solution pH.

* A value of at least 0·9912 is required for 0·001 level of significance.

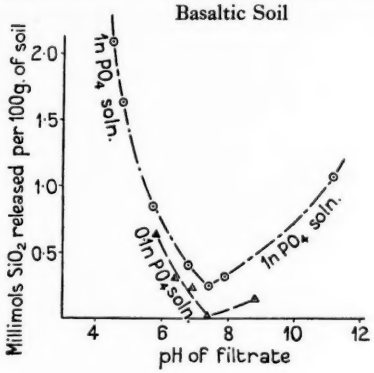

FIG. 1.

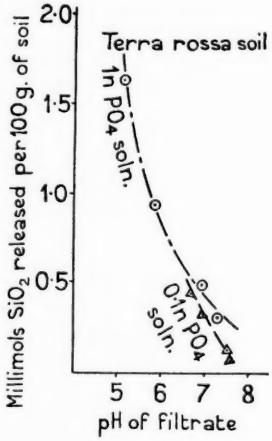

FIG. 2.

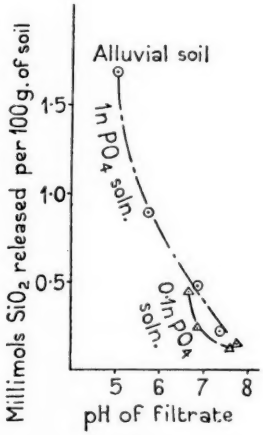

FIG. 3.

The data for the N/1 and N/10 solutions at the required filtrate-pH values were obtained by interpolation. With other factors constant, increasing the concentration of phosphate increased the silica release from the soil; but this increase in silica release in a 72-hour period was relatively small with respect to the increase in the phosphate concentration. That is, dilute solutions of phosphate are effective in displacing silica and the additional increments of phosphate in the solution are relatively much less effective. This may be in part due to the more concentrated solutions not attaining their maximum silica release as quickly as do the more dilute solutions.

(*d*) *Time*. In order to study the effect of time, the treatment was continued for varying numbers of days with basaltic soil (Table 7).

Although the rate of release was highest on the first day, the reaction continued with time. For the first 9 days the filtrate-pH values were more or less constant and the silica gradually rose. At 27 days and at 300 days there was a significant rise in pH and a depression in the silica.

TABLE 5

Release of Silica from Basaltic Soil by Sodium-phosphate Solutions of Different Concentrations at pH 6·00

Solution:soil ratio, 2½:1. Time, 72 hours.

Phosphate concentration	*pH of filtrate*	*Millimoles* SiO_2 *released per 100 g. of soil*
N/1	5·70	0·86
N/3	5·63	0·81
N/10	6·34	0·32
N/30	6·90	0·25

TABLE 6

Comparative Silica Release from Basaltic Soil where resulting Filtrate-pH Values are similar, while Phosphate Concentration varies

Solution:soil ratio, 2½:1. Time, 72 hours.

Filtrate pH of 5·63		*Filtrate pH of 6·90*	
Phosphate concentration	*Millimoles* SiO_2 *released per 100 g. of soil*	*Phosphate concentration*	*Millimoles* SiO_2 *released per 100 g. of soil*
N/1	0·91	N/1	0·36
N/3	0·81	N/10	0·25
N/10	0·70	N/30	0·25

TABLE 7

Effect of Time on Release of Silica from Basaltic Soil by Normal (M/3) Sodium-phosphate Solution of pH 6·00

Solution:soil ratio, 2½:1.

Period (days)	*pH of resulting filtrate*	*Millimoles* SiO_2 *released per 100 g. of soil*
1	5·60	0·73
3	5·70	0·86
9	5·70	1·07
27	6·20	0·82
300	6·61	0·69

It appears that there is a release of hydroxyl ions with time due to its liberation from free hydrous aluminium and iron oxides on chemically precipitating phosphate in the acid medium,

$$Al(OH)_3 + H_2PO_4^- \rightarrow Al(OH)_2H_2PO_4 + OH^-.$$

Thus, with a new H_3O^+-ion concentration, the silica level changes accordingly.

These results were for a solution:soil ratio of $2\frac{1}{2}:1$. It is expected that by considerably increasing this ratio, the silica release would tend more and more to approach a linear function with time. The reaction is a slow one and does not display the speed of a surface sorption or ordinary ion-exchange reaction.

TABLE 8

Effect of Solution:Soil Ratio upon the Release of Silica from Basaltic Soil by Normal (M/3) Sodium-phosphate Solution of pH 6·0

Time, 72 hours.

Solution:soil ratio	*pH of resulting filtrate*	*m.mol.* SiO_2 *released per 100 g. soil*	*g. soil per 100 ml. soln.*	*m.mol.* SiO_2 *released per 100 ml. soln.*
$2\frac{1}{2}:1$	5·70	0·86	40	0·344
10:1	5·92	2·44	10	0·244
25:1	5·98	3·75	4	0·150
100:1	5·99	5·64	1	0·056

Low and Black (1950) report an '8-day induction period' before this reaction started on kaolinite. Under the conditions of our experiments we failed to find any such tendency, having obtained an appreciable release of silica within a 1-day period with soils as well as with the clay minerals kaolinite, halloysite, illite, and montmorillonite.

(*e*) *Solution:soil ratio.* To observe the effect of varying solution:soil ratios, 200-, 50-, 20-, and 5-g. portions of basaltic soil were suspended in 500 ml. of M/3 sodium-phosphate solution of pH 6·0 and were allowed to stand 72 hours with occasional shaking. The results are given in Table 8 and Fig. 4. The amount of silica released per unit weight of soil increased as a logarithmic function of the volume of phosphate solution. It appears that with increasing amounts of solution the silica release in a 3-day period lags more and more behind the equilibrium value.

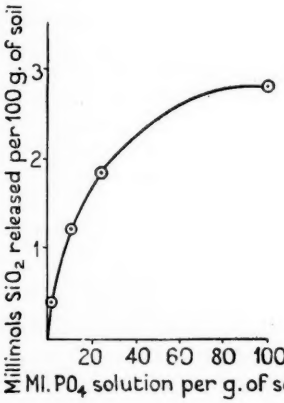

FIG. 4. Effect of solution:soil ratio upon silica release from basaltic soil by normal phosphate solution (pH 6) (72 hours).

The release of phosphate by silicate

Dilute (0·1 N) neutral solution of sodium silicate (neutralized with HCl) was found to be capable of releasing the fixed phosphate of the phosphated soils and clay minerals. That is, the reaction was reversible, except that with decreasing pH the effectiveness of the silicate in displacing

the phosphate anion decreased very rapidly and approached zero before reaching pH 4. With varying H_3O^+-ion concentration this displacing effect of the silicate anion behaves inversely to the displacing effect of the orthophosphate anion. Further, the inclusion of soluble silicate in the phosphate solution with which the soils and clay minerals were being treated depressed both phosphate fixation and the accompanying silica release. This effect of silicic acid in increasing phosphate availability has been reported by a number of workers, and to a large extent explains its beneficial effect upon plants and its ability to increase the efficiency of phosphate fertilizers (Hall and Morison, 1906; Lemmerman *et al.*, 1925; Gile and Smith, 1925; Reifenberg, 1930; Jessen and Lesch, 1930; Toth, 1939; Semb, 1943; Bastisse, 1950; Laws, 1951).

Summary

The orthophosphate anion was found capable of effecting a significant release of silica from soils and clay minerals, over and above the silica dissolved by water. The amount of silica released from different soils and clay minerals was compared. Finer-textured soils tended to release more silica than coarser-textured ones. The clay minerals showed an average silica release by neutral solutions of normal sodium and ammonium phosphate in the following order:

montmorillonite > halloysite > illite ⩾ kaolinite.

The influence of some factors affecting the reaction was studied. In the presence of Na^+ ions the silica release was greater than in the presence of NH_4^+ ions. The H_3O^+-ion concentration had a considerable influence. However, even at a neutral reaction the silica release from different soil material was significant. For the Israeli soils studied the release was least at *c.* pH 7·5, increasing at pH values above and below this. On the acid side the displacement of silica was accompanied by phosphate fixation. For final solution-pH values ranging from 4·5 to 7·4 the silica release from basaltic soil by normal sodium phosphate in 72 hours fitted the equation:

$$\text{Moles } SiO_2 \text{ released} = 0{\cdot}0569 \times [H_3O^+]^{0{\cdot}319}.$$

The release reaction was affected by the phosphate concentration, the solution : soil ratio, and time—the silica release increasing with each.

Neutral silicate in solution was in turn able to release the fixed phosphate, and its presence depressed the phosphate-retention silica-release reaction. With increasing H_3O^+-ion concentration its effectiveness decreased. This role of soluble silicate appears to explain to a large extent its reported benefit in soil fertility.

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LOSSES OF NITROUS OXIDE FROM SOIL

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IT has been suggested by a number of investigators that the gaseous loss of nitrogen from soils is a factor of some importance to agriculture. In nitrogen balance sheets, largely obtained from lysimeter experiments (see Russell, 1950, pp. 299, and Mann and Barnes, 1951), the deficits of nitrogen, which are loosely referred to as gaseous losses, are often large, particularly where high rates of application of nitrogenous fertilizer are used.

In the laboratory the process of denitrification whereby nitrates and nitrites lose nitrogen in the form of gas through the agency of micro-organisms is well known (Waksman, 1927, Chap. VII, Broadbent, 1951). It has, in fact, been known for many years that certain micro-organisms are able to liberate molecular nitrogen and nitrous oxide from cultures containing nitrate under a variety of conditions (Lloyd, 1931). Investigations along these lines have recently been reported by Verhoeven (1952), who used, under anaerobic conditions, a variety of aerobic spore formers, largely isolated from soil.

With natural soil there are considerable difficulties which beset the problem of deciding whether or not significant gaseous losses of nitrogen take place. Direct observations are required on the actual gaseous evolution of nitrogen and nitrous oxide before much further progress is possible. Because of analytical difficulties there is little that can be done to establish whether or not molecular nitrogen is evolved from natural soil in the comparatively small amounts anticipated. However, it is known that very small concentrations of nitrous oxide can be quantitatively dealt with by infra-red spectroscopic methods (Goody and Wormell, 1951). In this paper data on the rates of evolution of nitrous oxide are presented and the significance of the phenomenon to agricultural research is discussed.

Although very little information on the mechanism concerned in nitrogen loss was obtained from the examination of soil *en masse*, it was possible to consider some of the more general factors affecting the phenomenon, particularly in relation to the conditions likely to occur in nature.

Furthermore, the direct observational data on the release of nitrous oxide from soil was of value in furthering the geophysical problem of the origin of atmospheric nitrous oxide.

Experimental

Using an infra-red spectrometer and a 23-cm. absorption path it has been shown to be practicable to measure nitrous-oxide densities down to 2×10^{-8} g. cm.$^{-3}$, or approximately 30 times the density in the free atmosphere. The infra-red spectroscopic method for identifying and quantitatively estimating nitrous oxide has the advantage over chemical

and mass-spectrographic methods in that it is specific. The existence of a doublet band at 1,285 cm.$^{-1}$ of exactly the right shape tells beyond doubt that nitrous oxide is present (see Fig. 2). Water vapour absorbs slightly near 7·8 μ, and in order to avoid difficulty on this account a gas sample was always dried with phosphorus pentoxide and the spectrum compared with that of an evacuated tube. A 60° rock-salt prism of basal length 7 cm. was used in the spectrometer in a modified Littrow optical system. The detector was a Hilger Schwartz thermocouple used with an optical amplifier and photographic recording drum.

Soil airs from the field were obtained by burying perforated reservoirs of about 1-litre capacity and, after a suitable lapse of time, gas samples were withdrawn assuming that the contents of the reservoirs had come to equilibrium with the surrounding soil. Such a procedure has serious limitations, but was thought to be the most satisfactory of the simple techniques.

In order to examine a soil air under standard conditions and to concentrate the emitted gases, sealed vessels of a desiccator type (5–10 litres capacity), fitted with manometers and inlet tubes, were one-quarter filled with the soils. It was usual to start with freshly collected soil which had been dried by a cool stream of air so that ammonification and nitrification processes were reduced to a minimum; consequently the ammonium and nitrate contents were little above the values at the time of collection. Soils were used in a field state of aggregation and allowed to pack under their own weights. To obtain uniform wetting and even distribution of added nitrogen the required quantity of nitrogenous compound was dissolved in the calculated volume of distilled water which was added to the soil in such a manner as to obtain even wetting and, as far as possible, even application of solution, particularly when ammonium ions were added, because these ions would tend to undergo cation-exchange reactions at the point of contact with the soil. Provision was made for introducing oxygen into the systems if the partial pressures fell by 20 per cent. In all cases the oxygen tension was maintained at or near that of the free atmosphere. The carbon dioxide produced was removed by soda-lime contained in small open bottles placed on the soil surface.

Results

Preliminary tests made on nearly 50 soil-air samples collected from a variety of soils around Cambridge failed to show the presence of the minimum detectable amount of nitrous oxide (2×10^{-8} g. cm.$^{-3}$). However, in view of the fact that the gaseous diffusion in soil is ordinarily sufficiently rapid to renew the soil atmosphere several times a day (Penman, 1940) and that the conditions of the soils at sampling were not, as was subsequently found, the most favourable for nitrous-oxide formation, it was not surprising that the gas could not be detected. These results were contrary to those of Kriegel (1944) and Taylor *et al.* (1948), who claim to have measured considerable concentrations of nitrous oxide in soil air by chemical and mass-spectrographic methods, respectively. Such methods are not, however, specific, and examination

of these papers shows that the presence of nitrous oxide in the soil atmosphere has only been indicated and not proved. After the laboratory experiments reported herein had partially clarified the nature of the phenomenon under investigation it was a simple matter to demonstrate conclusively the presence of nitrous oxide in a soil atmosphere in the field.

In view of the well-known bacterially induced formation of nitrous oxide from nitrate in suitable culture, the effect of adding increasing amounts of water to a nitrate-containing soil on the nitrous-oxide content of the soil atmosphere was studied. The experiments were performed in the sealed desiccator-type vessels in which the atmospheres were maintained at oxygen tensions at or near ordinary free-atmosphere tension. When nitrous oxide was detected the results showed an approximately linear increase of the concentration of the gas with time for the duration of the experiments (between 3 and 66 hours, depending on whether the nitrous-oxide evolution was large or small) and also rough proportionality between nitrous-oxide release and the available nitrogen (nitrate and ammonium, *vide infra*) for concentrations ranging up to about 50 parts of nitrogen per million of dry soil. It is assumed that these linear relationships are generally true, and hence the results of each experiment have been reduced to a time constant (τ in days) which defines the initial rate of transformation of the available nitrogen in the soil into nitrogen as nitrous oxide appearing in the atmosphere. Thus, for example, if a g. dry soil contain b p.p.m. of available nitrogen, the meaning of the time constant is that the initial rate of evolution of nitrous oxide is

$$\frac{a \times b \times 10^{-6}}{\tau} \text{ g. nitrogen per day.}$$

The results for the first experiments are recorded in Table 1.

TABLE 1

Sandy loam from Hinton Hall (pH 5·4), Arable. 25 p.p.m. nitrogen added as $NaNO_3$. *Amounts of Nitrate and Ammonium Nitrogen already present were* <2 *p.p.m. Temp. 16° C.*

Mass of moisture / Mass of dry soil	0·15	0·20	0·25	0·30	0·35
τ days	>770	500	76	24	17

Two other soils examined, namely, a Kimmeridge light clay soil (pH 7·7) and a Clay-with-Flints soil (pH 7·3), both cultivated, were wetted to moisture contents (mass of water: mass of dry soil) of 0·42, and gave values of τ of 18 and 6 days, respectively, for 25 p.p.m. nitrogen added as sodium nitrate at 21° C. These soils contained large amounts of water and, for practical purposes, the individual soil aggregates could be said to be saturated.

The effects of increasing water contents on the nitrous-oxide release from a soil to which ammonium ions, as ammonium chloride, had been

added are summarized in Fig. 1. The values for τ show a minimum of 23 days at a moisture content of about 0·35 in an arable medium loam (pH 7·0). At moisture contents below about 0·15 the nitrous-oxide release probably stopped altogether; in any case it was indeterminably

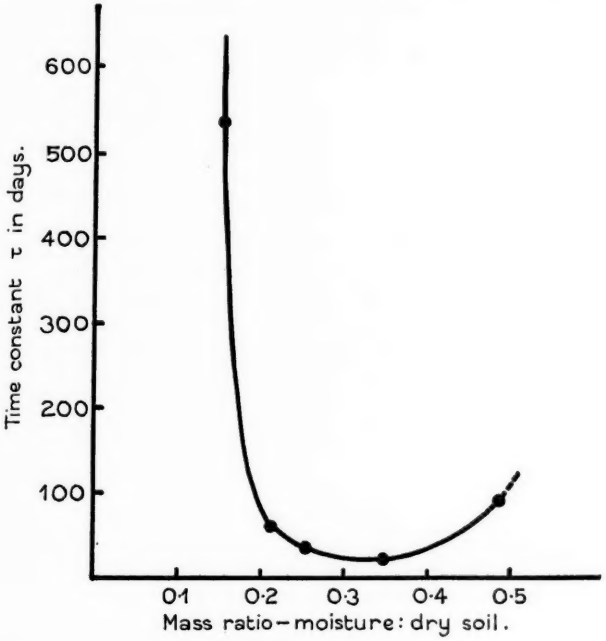

FIG. 1.

small. This soil contained negligible natural ammonium- and nitrate-nitrogen contents. The effects of increasing the moisture contents of soil was further examined by taking a Fen Peat (pH 8·0) and adding to it small amounts of ammonium nitrogen and a variable amount of water. Values of τ derived from the added nitrogen and the nitrous oxide released were >600, >600, 280, and 13 for moisture contents of 0·6, 0·8, 0·9, and 1·0, respectively. It need hardly be mentioned that the usual range of moisture contents in peaty soils is very much higher than in mineral soils.

In very wet soils rather inconsistent results were obtained, and in most soils it did not seem to matter much whether the added nitrogen was in the form of nitrate or ammonium ions; provided the moistures were sufficiently high, nitrous oxide was produced. At the high moisture contents the principal difficulty lay in attempting to obtain even wetting of the soil. In general it may be said that nitrate nitrogen resulted in a greater evolution of nitrous oxide than did ammonium nitrogen, as is illustrated in Table 2.

TABLE 2

Arable Medium Loam (pH 6·5) from Cambridge University Farm. Moisture content 0·32 (soil drained at tension of about 5 cm. H_2O, *i.e., a very wet soil, practically saturated). Soil contained 8 p.p.m. nitrate-*N, *but negligible ammonium-*N. *Temp. 18° C.*

Nitrogen added to the soil	*τ days*
None	53
None	30
60 p.p.m. as $NaNO_3$	93
30 p.p.m. as $NaNO_3$	65
60 p.p.m. as $(NH_4)_2SO_4$	130
30 p.p.m. as $(NH_4)_2SO_4$	110

Using soil which had been under long-established grass cover it was found that losses of nitrogen as nitrous oxide of the order of the ones recorded in Table 2 took place at moisture contents which, although apparently higher than for arable soil of comparable texture, were moisture contents which corresponded to greater tension, e.g. of the order of 50 cm. H_2O. The results are recorded in Table 3. When the moisture content (0·43) of this soil was that which corresponded to a pF of 2·0 (Schofield, 1935) the rate of nitrous-oxide evolution was approximately one-tenth that at 0·50 moisture content.

TABLE 3

*Welsh Silty Loam under Permanent Pasture (pH 5·3–5·5). Moisture content 0·50 (pF 1·65). Approximately 5 p.p.m. nitrate-*N *and 1 p.p.m. ammonium-*N *present. Temp. 18° C.*

Nitrogen added to the soil	*τ days*
None	15
40 p.p.m. as $NaNO_3$	17
40 p.p.m. as $(NH_4)_2SO_4$	45
20 p.p.m. as $(NH_4)_2SO_4$	25

Experiments carried out on an acid soil (pH 4·7) of Clay-with-Flints origin under permanent grass gave the results recorded in Table 4. It appeared that in this soil the added ammonium nitrogen made no difference to the evolution of nitrous oxide. Presumably the ammonium ions remained unchanged in this acid soil. Apart from this single remark bearing on the influence of soil pH on nitrous oxide evolution, no definite conclusions on the general influence of pH were drawn. From data which are not reported, the inference was that nitrous-oxide evolution increased with falling pH values (6·8 to 5·6), however, this aspect of the problem deserves further attention.

Experiments were performed to examine further the evolution of nitrous oxide as a product of the metabolism when soil contained comparatively small amounts of moisture and was, as in the previously described experiments, in contact with an atmosphere containing oxygen

TABLE 4

Clay-with-Flints Soil (pH 4·7) under Grass. Moisture 0·50, corresponding to a tension of about 8 cm. H_2O, which meant that the soil was quite near saturation. Soil contained 4–5 p.p.m. nitrate-N, but negligible ammonium-N. Temp. 18° C.

Nitrogen added to the soil	*τ days*
None	32
None	28
40 p.p.m. as $NaNO_3$	120
20 p.p.m. as $NaNO_3$	45
40 p.p.m. as $(NH_4)_2SO_4$	290
20 p.p.m. as $(NH_4)_2SO_4$	170

at or near ordinary free-atmosphere tension. For this the arable medium loam (pH 7·0) which contained negligible natural ammonium- and nitrate-nitrogen contents was used, as in the experiments summarized in Fig. 1. At a moisture content of 0·16, corresponding to a pF $>$ 2·0, detectable amounts of nitrous oxide were obtained when the added nitrogen was in the form of ammonium ions or urea. No nitrous oxide was detected in the atmosphere when nitrate nitrogen alone was added to the soil at the 0·16 moisture content. The data are summarized in Table 5.

TABLE 5

Arable Medium Loam (pH 7·0) from Cambridge University Farm. Moisture content 0·16, corresponding to pF $>$ 2·0. Temp. 16° C.

Nitrogen added to the soil	*τ days*
26 p.p.m. as NH_4Cl	330
26 p.p.m. as NH_4NO_3	670
26 p.p.m. as $NaNO_3$	$>$ 3,000
26 p.p.m. as urea	340

From the results so far obtained it was concluded that it should be possible to detect nitrous oxide in the soil atmosphere in the field under suitable conditions. Accordingly, a site was chosen in the sandy loam at Hinton Hall and a pit was dug 70 cm. × 70 cm. and 50 cm. deep and two open-ended cylindrical earthenware pipes, each of one litre volume, were buried horizontally at each of three depths, 12·5, 25, and 40 cm. As the soil was returned to the pit a dilute solution of ammonium sulphate was sprayed on so that the soil was uniformly wetted and contained 8 p.p.m. of added nitrogen.* Samples of the soil atmosphere were withdrawn from the buried reservoirs after 1, 4, 7, and 11 days. Large quantities of nitrous oxide were detected on all occasions, and the individual spectra for the fourth day are shown in Fig. 2, together with a comparison spectrum of nitrous oxide. The composite results

* This amount of ammonium sulphate if applied as a surface dressing would correspond to 4 cwt. per acre, which is a normal agricultural dressing for some crops.

for all four occasions are shown in Fig. 3. The rapid decline of activity between the fourth and eleventh day could have been due to the drying

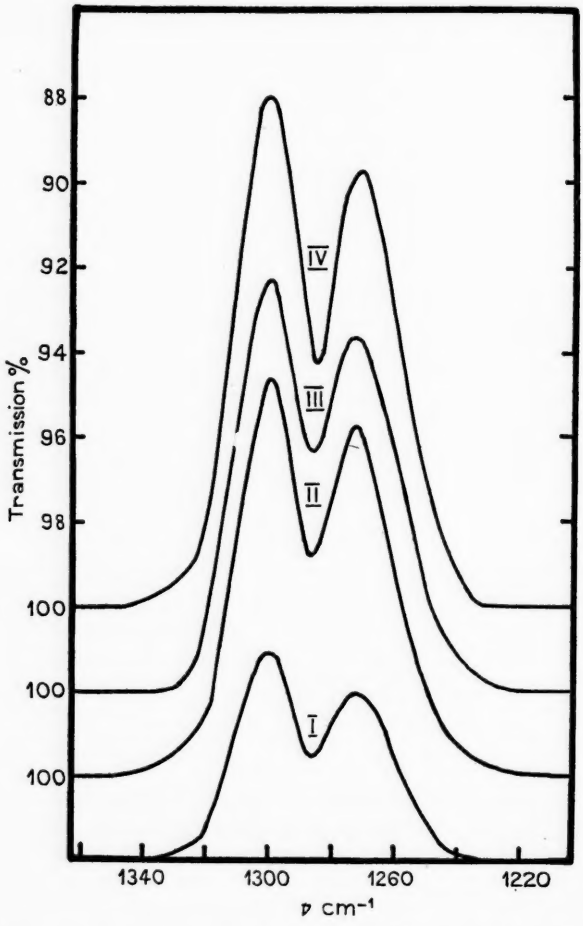

FIG. 2. Absorption spectra of soil air from Hinton Hall 4 days after the start of the field experiment. Soil temp. 21° C. at surface (noon), 18° C. at 30 cm. Moisture content (average) about 0·21. 8 p.p.m. of added nitrogen as $(NH_4)_2SO_4$. I. 40-cm. depth. II. 25-cm. depth. III. Comparison spectrum of $3{\cdot}85 \times 10^{-5}$ g. cm.$^{-2}$ N_2O at a total pressure of 665 mm. Hg. IV. 12·5-cm. depth.

out of the soil (moisture about 0·16–0·17 on eleventh day) or to the depletion of the available-nitrogen content. It was most likely to be a combination of both factors.

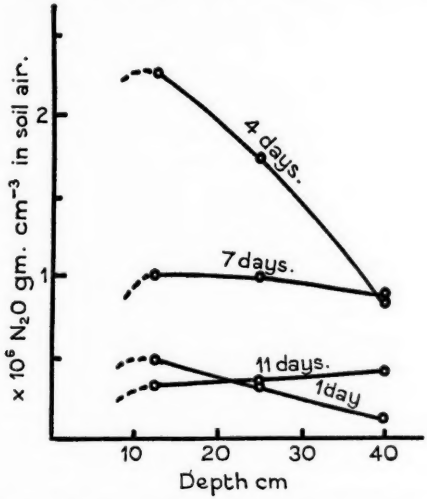

FIG. 3. Nitrous-oxide concentrations at Hinton Hall, 3 to 14 July 1952.

Discussion

All the soils examined in the laboratory showed nitrous-oxide evolution under some or other conditions, one factor, namely the oxygen tension in the atmosphere over the soil, being regulated at or near free atmospheric-oxygen tension. Perhaps the most striking observation was on the effect of increasing the moisture contents of soils on the nitrous-oxide evolution (see Table 1, Fig. 1, &c.). When soil is extremely wet and individual aggregates are approaching saturation, it appears that nitrous oxide is evolved in considerable quantity if any readily available nitrogen is present. Values of τ down to 10 days or less were encountered, which means that nitrous-oxide evolution alone would almost completely deplete the soil of available nitrogen in periods of the order of 10 days under the near-saturation conditions. There can be very little doubt that large amounts of moisture tend to restrict the free diffusion of oxygen through the soil mass. This part of the problem is too difficult to deal with in any quantitative fashion at present, as it would involve, among other things, a critical examination of the soil structure-moisture content relationships, upon which the aeration of soil must to a large extent depend. As moisture contents decreased, the values for τ increased rapidly, values in the region of 300 being measured in some soils at pF values of about 2·0.

In most instances when soil was approaching saturation with moisture it did not much matter whether nitrate or ammonium nitrogen was present; nitrous oxide was evolved in large amounts. In general, nitrate nitrogen was somewhat more liable than ammonium nitrogen to result in nitrous-oxide evolution. In very acid soil (pH 4·7) ammonium ions

did not appear to contribute to the nitrous-oxide production. Presumably the ammonium ions did not undergo any changes in the acid soil.

Where large evolutions of nitrous oxide were obtained after nitrate had been added to a soil, the results were in accordance with the view that nitrate is liable to be reduced to nitrous oxide (and molecular nitrogen and ammonium ions—Verhoeven, 1952) under conditions which tend towards anaerobic. Increasing water contents in soil result in more and more pronounced anaerobic conditions and, in general, a consequent increasing nitrous-oxide evolution. At first sight one might be tempted to assume that nitrous oxide always arises from nitrate, which ion may, of course, form from ammonium ions during the conduct of an experiment. However, it is interesting to note that when a moisture content was not large enough to permit nitrate nitrogen to cause the evolution of nitrous oxide (see Table 5) it was possible to detect nitrous oxide if ammonium nitrogen or urea (which is known to be easily ammonified) was present in the soil. A value for τ of the order of 300 days was measured for added ammonium nitrogen at the comparatively low moisture content. Calculation showed that under the experimental conditions prevailing in the medium loam (pH 7·0) when ammonium nitrogen was present at the 0·16 moisture content ($pF > 2{\cdot}0$), about 2–3 per cent. of the ammonium nitrogen which disappeared (nitrified, &c.) during the course of the experiment appeared as nitrous oxide in the soil atmosphere. The simplest explanation of this result would be that nitrous oxide appears during the oxidation of ammonium ions when the oxygen supply is somewhat limited. As far as is known, this suggestion has not received any support before, and, perhaps, some other explanation should be sought for the evolution of the gas under these conditions. It was, however, fairly clear that the soil in question was not wet enough for the production of detectable amounts of the gas from nitrate. When this soil contained less than 0·15 moisture the nitrous-oxide concentration did not reach detectable levels in any experiment.

Even if the formation of nitrous oxide from nitrate is dissimilatory reduction by micro-organisms, the over-all conversion $NH_4^+ \rightarrow N_2O$ may take a number of possible paths. It must be admitted that some of the ammonium ions may be transformed to nitrite or nitrate and then be reduced, but the results in Table 5, obtained at moderately low moisture content, suggest some other mechanism operates as well. It is noteworthy that the author found in an isolated observation that hydroxylamine added to a wet soil produced very large evolutions of nitrous oxide. It has been suggested that hydroxylamine is an intermediary in the changes $NH_4^+ \rightarrow NO_2'$ (Blom, 1928); thus where the oxygen supply is limited the oxidation of ammonium ions may yield hydroxylamine which, in the absence of sufficient oxygen, does not all become further oxidized, but interacts with accumulated nitrite to yield nitrous oxide.

$$NH_2OH + NO_2' \rightarrow N_2O + H_2O + OH'.$$

Such a reaction does slowly take place in neutral and slightly alkaline

conditions (phosphate buffer, pH 7·5) as well as in acid and slightly acid conditions at concentration levels of M/500 with respect to both interactants, even at room temperature (author's observation). The interaction of hydroxylamine and nitrite, although slow, would explain why the former is seldom, if ever, found in soils in which it is well known that at least small amounts of nitrite may accumulate.

General Implications

The results indicate that an almost immeasurably slow release of nitrous oxide can take place at moderate moisture contents (pF values of the order 2·0), while under extremely wet conditions large releases of the gas are likely. It is to be expected that nitrous-oxide evolution would be a seasonal phenomenon related to the available-nitrogen content of the soil, the degree of aeration, and probably the supply of easily decomposable organic matter, the soil pH, and the temperature, to mention the most obvious factors.

From the soil-fertility side of the question it does not matter whether the gaseous escape is of nitrous oxide or molecular nitrogen. Insufficient aeration, whether caused by excess moisture or by inferior soil structure in conjunction with sufficient moisture to render the environment reducing, can lead to a gaseous escape of nitrous oxide and presumably molecular nitrogen. It is probably enough that the conditions tend towards the anaerobic. A state may be visualized in which the rate at which oxygen is being used is not quite being made good by diffusion to the more inaccessible centres. From one of Verhoeven's (1952, p. 112) remarks, 'under conditions commonly designated as aerobic in bacteriological practice, to wit in a shallow layer in a cotton-plugged flask', it is clear that this author seriously doubts whether ordinary bacterial-culture technique is aerobic. Verhoeven shows that an aerated shake technique is necessary to inhibit nitrous-oxide and nitrogen evolution in his enrichment culture experiments. Such statements as Meiklejohn's (1940), 'it is very difficult to eliminate denitrification by means of increased aeration', provide further evidence about the difficulty of avoiding conditions favouring denitrification in bacterial cultures. It is apparent that there exists a certain amount of confusion as to whether anaerobic conditions are necessary or not for denitrification to take place. To the present author's mind the difficulties are inherent in static bacterial-culture techniques which involve layers of liquid or colloidal medium of finite thickness. In the experiments briefly described in this paper it appears that oxygen deficiency is required before nitrous oxide is produced from soil. In well-aerated soils even at rather high moisture contents, no detectable release of nitrous oxide was encountered. However, as Winogradsky (1926) states, even when a soil is far from saturated with moisture, anaerobic organisms find conditions favourable for their development at the very surface of the soil. In soil in the natural state one may expect that the damping of aggregates in the normal course of absorbing rainfall will create a medium favourable for gaseous loss of nitrogen as both molecular nitrogen and nitrous

oxide. It is pertinent that nitrate nitrogen is regarded as the most fugitive constituent of the soil; after accumulating fairly steadily, it may rather suddenly begin to disappear. The system is obviously complicated, because during its disappearance the nitrate may be assimilated by plants, by micro-organisms, be reduced to ammonium ions, to nitrous oxide, and to nitrogen, and possibly escape as other oxides of nitrogen (Gerretsen, 1950) or even as ammonia provided the soil is on the alkaline side of neutrality (Jewitt, 1942, van Schreven, 1950).

In view of the varying proportions of N_2 to N_2O obtained by Verhoeven (1952) in his enrichment cultures it would be impossible at present to hazard a guess as to the range of the ratio N_2/N_2O in the gas evolved from soil. It is probably a most variable ratio, but the results of the experiments reported suggest that the nitrous oxide is an important constituent under natural conditions. When an environment is truly anaerobic, molecular nitrogen may be the sole product of denitrification (Jones, 1951).

In the same way that it might be possible to underestimate denitrification losses because of concomitant nitrogen fixation, particularly by anaerobic organisms, it is equally possible that nitrogen-fixation studies have underestimated the nitrogen fixed because of significant denitrification taking place concurrently in the soil containing the mixed micro-organism population (see, for example, Jensen and Swaby, 1940).

In so far as fertilizer usage is concerned it is apparent that very large losses of nitrogen are likely to take place as nitrous oxide alone in a thoroughly wet soil following the application of easily available nitrogen. In agricultural practice one sees another good reason for attending to badly drained lands and for maintaining and, where possible, improving soil structure. The benefits of adequate aeration in soils will be reflected in their nitrogen economy. Clearly, further investigation is required into this most important question. It is suggested that the criterion of nitrous-oxide evolution might well be used for deciding if a soil is insufficiently aerated; such an assay would be a biological one, and have much to commend its use.

Geophysical implications

It is of geophysical interest to show whether it is possible for bacterial reactions in the soil to supply the atmosphere with its observed nitrous oxide (Adel, 1951). According to the data of Prasolov (1946) soil, other than tundra, desert, &c., covers 0·16 of the surface of the earth. From a general consideration of soil-profile data it appears that the depth of biologically active top-soil which is in equilibrium with the atmosphere is usually within the range 10–100 cm. (Glinka, 1927). We shall take 30 cm. as a reasonable value for its mean depth and 1·5 as its density. The experiments described herein suggest that in wet soil both nitrate and ammonium nitrogen should be considered as potential sources of nitrous oxide. The concentrations of nitrogen in soils in these forms is highly variable (Russell, 1950, pp. 291–4), but usually lie within the range 1 to 100 p.p.m. Taking the average value (NO_3^- plus NH_4^+-

nitrogen) as 10 p.p.m.* the above figures give for the available nitrogen molecules per cm.$^{-2}$ of the total earth's surface

$$\frac{0{\cdot}16 \times 30 \times 1{\cdot}5 \times 10^{-5} \times 6{\cdot}0 \times 10^{23}}{28} = 1{\cdot}6 \times 10^{18} \text{ molecules cm.}^{-2}.$$

The mean destruction rate of nitrous oxide in the atmosphere has been estimated to be 8×10^{10} molecules cm.$^{-2}$ sec.$^{-1}$ (Goody and Walshaw, 1953). In order to achieve such a rate of supply we would therefore require a reaction with a time constant of $2{\cdot}0 \times 10^{7}$ seconds, or about 230 days, subject to an uncertainty of about one order of magnitude. Owing to the non-linear dependence of the measured time constant upon moisture content and the great variability of rainfall and of the moisture-holding capacity of soils, it has proved very difficult to make an estimate of the mean time constant of soil surfaces which would be acceptable even to one order of magnitude. The relevant facts are that under very wet conditions the time constant can be of the order of 10 days and that for fairly wet conditions the order of magnitude is 100 days. After careful consideration of such data as are available the conclusion has been reached that the periodic wetting of soil surfaces by rainfall would lead to an expected time constant of the order of 100 to 1,000 days, and therefore that soil surfaces are certainly a possible source of supply of atmospheric nitrous oxide.

This has been discussed further by Goody and Walshaw (1953), who show that the soil surfaces are probably the source of the major part of the atmosphere's nitrous oxide.

Summary

Data obtained from infra-red spectra of soil airs collected both in laboratory experiments and in the field indicate that nitrous-oxide evolution is a factor of considerable significance to the nitrogen economy of soils.

Soils which are approaching saturation with moisture rapidly release large amounts of their available nitrogen as nitrous oxide; at lower moisture contents very slow evolution of the gas can take place.

The soils of the earth are shown to be a very possible source of supply of atmospheric nitrous oxide.

Acknowledgement

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THE REDUCTION OF IRON OXIDE BY BACTERIA

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HALVORSON and Starkey (1927) found that a mixed soil inoculum, or a culture of *Escherichia coli* or *Clostridium sporogenes*, could reduce ferric hydroxide under anaerobic conditions in a 1 per cent. glucose-mineral-salts medium or 1 per cent. peptone medium, and that reduction was greatest in the glucose medium inoculated with soil or *E. coli*. Roberts (1947), on the other hand, found after testing 265 cultures of soil micro-organisms that only freshly isolated strains of *Bacillus polymyxa* from soil were capable of reducing iron in a 1:10 aqueous soil suspension containing 0·5 per cent. glucose. He observed extensive reduction of ferric hydroxide and iron in soil colloids with *B. polymyxa* isolates in glucose media.

The possible connexion between the activities of iron-reducing bacteria and the gleying of clay has been commented on by Allison and Scarseth (1942) and by Bloomfield (1950). Bloomfield (1951) suggested that plant products are in part responsible for the gleying process.

In view of the conflicting results of Halvorson and Starkey (1927) and Roberts (1947) the work described below was carried out

(1) to determine the types of bacteria that could reduce iron oxide;
(2) to determine the amount of reduction produced by these bacteria in various media;
(3) to determine whether iron-reducing bacteria were present in gleyed clay at 10 ft.;
(4) to obtain reduction in sugar media at pH values higher than reported by Bloomfield (1950), namely 3·5–4·5; and
(5) to study aspects of iron reduction by pure cultures.

Source of Isolations

Bacteria were isolated from:

(1) Bones Close soil, Rothamsted, a light brown clay, pH 7·1, 1 to 6 in. sample, which had been partly artificially gleyed with sugar (Allison and Scarseth, 1942; Bloomfield, 1950);
(2) a naturally gleyed soil under peat from moorland near Bolton, Lancs.; and
(3) fermenting grass.

The Bones Close soil, 5 g., was moistened with 4 ml. of 2·5 per cent. sucrose solution and incubated anaerobically for 7 days at 30° C. The soil was then suspended in 10 ml. of sterile distilled water and bacteria were isolated from it.

The naturally gleyed soil, collected from a depth of 2 ft., was used directly to inoculate a liquid medium, found suitable for testing iron reduction, and bacteria were isolated from the crude culture which developed under anaerobic conditions.

Fresh grass, 15 g., and 1 g. of $(NH_4)_2SO_4$ in 100 ml. of sterile tap-water were incubated anaerobically for 7 days at 30° C, and bacteria were isolated from the liquor.

Media used for Isolations

Soil-extract medium. This medium was similar to that used by Roberts (1947) except that glucose was replaced by the non-reducing sugar, sucrose. The medium consisted of the following: Bones Close soil, 20 g.; sucrose, 2·0 g.; NH_4Cl, 0·8 g.; agar, 5·0 g.; distilled water, 250 ml. The Bones Close soil was boiled in 250 ml. of distilled water for 30 minutes and the supernatant, which contained the colloidal fraction of the soil, decanted. The volume of the supernatant was made up to 250 ml. with distilled water and the rest of the constituents added, and the pH adjusted to 7·2. The medium was autoclaved at 15 lb./sq. in. for 15 minutes.

Grass-extract medium. Fifty grammes of fresh grass was boiled for 2 hours in 500 ml. of distilled water and the liquor was clarified through a Seitz filter. Ferric hydroxide, precipitated from solution of ferric chloride and sodium hydroxide and washed 6 times with distilled water to remove electrolytes, was added to the grass extract at the rate of 0·5 g. per 500 ml. The medium was adjusted to pH 7·0 and 2 per cent. agar added and autoclaved at 15 lb./sq. in. for 15 minutes.

Medium A. KH_2PO_4, 0·05 g.; $MgSO_4.7H_2O$, 0·02 g.; $(NH_4)_2SO_4$, 0·1 g.; sucrose, 0·5 g.; $CaCO_3$, 0·5 g.; $Fe(OH)_3$, 0·05 g.; Difco yeast extract, 0·015 g.; distilled water, 100 ml. When necessary the medium was solidified with 2 per cent. agar. The medium was adjusted to pH 7·0 and autoclaved at 15 lb./sq. in. for 15 minutes.

Method of Detecting and Isolating Iron-reducing Bacteria

The reduction of iron by bacteria in the various media was detected with a 0·1 per cent. solution of $\alpha\alpha'$ dipyridyl in 10 per cent. acetic acid, which turns red in the presence of ferrous iron. Reduction was considered to have taken place on solid media when strips of filter-paper soaked with $\alpha\alpha'$ dipyridyl solution immediately turned red when placed over the growth; and in liquid media when the addition of $\alpha\alpha'$ dipyridyl solution caused an immediate reddening of the culture. It was hoped that the colonies of iron-reducing bacteria would stain red with $\alpha\alpha'$ dipyridyl, but the inoculated medium turned a uniform pink and showed no localized sites of reduction.

When isolations were made under anaerobic conditions the plates were incubated in anaerobic jars which had been evacuated for 10 minutes and filled with nitrogen. Reduced methylene blue was placed in each jar to check anaerobiosis. All the isolations were made at 30° C.

Inocula from Bones Close suspension and grass liquor were plated on to soil- and grass-extract media respectively, and incubated aerobically and anaerobically. The anaerobic plates gave a good test for ferrous iron, and single, isolated colonies were picked off untreated plates and inoculated on to slopes of similar media and incubated anaerobically for 7 days. One slope of each isolate was tested for ferrous iron, and cultures of those which gave a good test were retained.

Inocula from the gleyed clay were added to liquid medium *A*, and a good test for ferrous iron was obtained in this medium incubated either aerobically or anaerobically. Single colonies were isolated on solid medium *A* from platings of the anaerobic cultures and inoculated into tubes of liquid medium *A*. The cultures were tested for ferrous iron after 7 days, and to test the purity of the positive isolates plates of medium *A* were inoculated with the growth in duplicate cultures of the isolates.

About 30 cultures were isolated from the three sources and all except three grew well on solid medium *A* under aerobic conditions.

Identification of the Isolates

Biochemical tests were made on the isolates and 10 different cultures were obtained. The isolates were placed into genera using Skerman's key (1949) and checked by descriptions in Bergey's *Manual of Determinative Bacteriology* (1948). The isolates belonging to the genus *Bacillus* were studied as recommended by Smith *et al.* (1946).

The isolates included members of the following genera: *Escherichia*, *Aerobacter*, *Bacillus*, and *Paracolobactrum*.

Reduction of Iron by Isolates in Various Media

Roberts (1947) claimed that *B. polymyxa* was the only micro-organism which reduced iron to any extent, and yet Halvorson and Starkey (1927) found several years earlier that *E. coli* caused marked reduction in sugar medium. It was decided therefore to test the various isolates in a number of different media.

Media used for iron reduction.

1. Roberts's medium (1947); K_2HPO_4, 0·31 g.; KH_2PO_4, 0·08 g.; KCl, 0·02 g.; $MgSO_4.7H_2O$, 0·02 g.; asparagine, 0·5 g.; glucose, 2·4 g.; distilled water, 100 ml.; pH, 7·0.
2. Peptone, 1 g.; distilled water, 100 ml.; pH, 7·0.
3. Soil extract, 100 ml.; sucrose, 0·8 g.; NH_4Cl, 0·32 g.; pH, 7·0.
4. Halvorson and Starkey's medium (1927): $(NH_4)_2SO_4$, 0·01 g.; K_2HPO_4, 0·01 g.; $MgSO_4.7H_2O$, 0·001 g.; $CaCl_2$, 0·001 g.; glucose, 1·0 g.; distilled water, 100 ml.; pH, 7·2.
5. Medium *A*: the same composition as given earlier.

Method for Determining Iron Reduction

The various media were dispensed in 25-ml. portions into 6 in. × 1 in. boiling tubes and sterilized, and when cool 1 ml. of sterile suspension of ferric hydroxide (0·01 g.) was added to each tube. The media were inoculated with 1 drop of a suspension of a 48-hour slope culture and incubated anaerobically for 5 days. Ferrous iron in the supernatant was determined as follows: a 5-ml. aliquot of the culture was pipetted into a 100-ml. volumetric flask, to this 1 ml. of 0·2 per cent. solution of $\alpha\alpha'$ dipyridyl in 10 per cent. acetic acid was added, and then glass-distilled water added to the 100 ml. mark. The solution was centrifuged to clear it of suspended bacteria and the intensity of colour of the cleared

solution measured in a Spekker colorimeter using a 604 green filter. From a standard calibration curve the readings were converted to concentrations of ferrous iron expressed as mg. per litre. The pH values of the cultures of the various bacteria were measured, using a glass electrode.

Results

The amount of ferrous iron in solution and the pH of the cultures of the various bacteria are given in Table 1.

TABLE 1

Showing Amounts of Ferrous Iron (mg. per litre) in Solution and Final pH Values in Various Media which were inoculated with Various Bacteria and incubated anaerobically for 5 Days at 30° C.

	Medium inoculated											
	Soil extract		*Halvorson and Starkey's*		*Roberts's*		*1% Peptone*		*Roberts's sucrose*		$CaCO_3$ *medium A*	
	pH values and ferrous iron in solution (mg./l.) average of 2 determinations											
Bacteria tested	*pH*	*Fe*	*pH*	*Fe*	*pH*	*Fe*	*pH*	*Fe*	*pH*	*Fe*	*pH*	*Fe*
Escherichia freundii	3·6	19	4·3	9	5·2	10	6·8	1	4·1	13	6·4	3
Bacillus polymyxa (*i*)	4·1	7	6·2	1	5·8	6	6·8	1	6·0	4	6·1	20
Bacillus cereus	5·0	3	6·3	1	6·7	7	6·9	1	6·5	2	7·0	0
Bacillus megaterium	4·5	3	6·3	1	6·8	6	6·9	1	6·6	2	7·0	1
Aerobacter aerogenes	3·7	3	4·0	16	4·8	9	6·9	1	4·7	3	6·4	9
Bacillus polymyxa	4·5	5	6·2	1	6·4	7	6·9	1	6·5	5	6·0	25
Aerobacter (*ii*)	3·6	16	4·2	15	5·0	10	7·1	1	5·1	20	6·4	2
Paracolobactrum	4·2	4	4·6	15	5·4	4	7·2	1	5·1	10	6·5	4
Bacillus circulans	..	..	6·2	1	..	..	7·0	1	6·5	10	5·8	40
Control	5·0	4	6·3	1	7·4	4	7·1	1	6·6	2	7·0	0

The *Bacillus polymyxa* strains and *Bacillus circulans* gave good reduction in medium *A* but fair to no reduction in the other media. *Escherichia* and *Aerobacter* (*ii*) gave fair reduction in Halvorson and Starkey's medium, soil extract medium, and Roberts's medium. *Aerobacter* (*i*) and to a lesser extent *Paracolobactrum* gave fair reduction in Halvorson and Starkey's medium. *Bacillus cereus* and *Bacillus megaterium* did not reduce significant amounts of iron in any medium. The *B. megaterium* and *B. cereus* were not isolated as iron-reducing bacteria but were studied for comparison. None of the bacteria reduced iron to any extent in 1 per cent. peptone medium.

Species of *Escherichia*, *Aerobacter*, and *Paracolobactrum* reduced iron best in media in which the pH value fell to a low figure, whilst *B. polymyxa* and *B. circulans* reduced iron in media whose pH did not fall below values of 5·5–6·0. A more detailed comparison is not possible because some isolates did not grow in all media. All the isolates, however, grew well in medium *A*.

Reduction of Iron present in Soil by Various Bacteria

To determine whether the various isolates could reduce the iron compounds present in soil, 10 g. samples of sterile Bones Close subsoil were moistened with 4 ml. of a suspension of the test organism in

medium *A* or 4 ml. of the medium alone and were incubated anaerobically for 7 days at 30°. The soils were then suspended in 10 ml. of distilled water and tested for ferrous iron with $\alpha\alpha'$ dipyridyl. Ferrous iron was detected in the soils which were inoculated with *B. circulans* and in uninoculated fresh soil but not in soils which received any of the other isolates or the sterile medium alone.

Occurrence of Iron-reducing Bacteria in Gleyed Clay

The clay used in this experiment was collected from a clay pit near Preston, Lancs. The clay at a depth of 2 ft. exhibited extensive gleying along and in from the structure faces of the clay elements and root channels; whilst at 10 ft. it showed only superficial gleying on structure faces.

Samples of the gleyed material which had been taken aseptically from uncontaminated surfaces of structure elements from 2 and 10 ft. were weighed out in 1·0 g. lots and suspended in 10 ml. of sterile distilled water. Serial 1/10 dilutions were made from these suspensions in 6 in. $\times \frac{3}{4}$ in. test-tubes containing 9 ml. of sterile medium *A*. Plates of medium *A* solidified with 2 per cent. agar were inoculated with 1 ml. of these dilutions and the plates and the remainder of the dilutions incubated aerobically and anaerobically for 6 days at 30° and then examined for ferrous iron and growth.

The results described below are those obtained using samples of two clay profiles which were collected on different occasions. The dilutions of gleyed clay from 10 ft. in both samples did not produce growth on the plates or in the liquid medium and did not reduce iron. With the clay from 2 ft., growth was obtained on plates which received 10^{-5} and 10^{-6} dilutions of the first and second samples respectively, and reduction and growth occurred in the liquid medium at dilutions of 10^{-7} of both. The reduction of iron appeared to be slight in dilutions greater than 10^{-4}.

Studies on Iron Reduction with B. circulans *and* B. polymyxa

Reduction in the presence of various substrates. Sucrose was replaced in medium *A* by 0·5 per cent. peptone, asparagine, glycine, ethyl alcohol, glycerol, sodium lactate, sodium malate, sodium citrate, glucose, or fructose. The medium was also prepared without any organic carbon source. These substrates are those which enable *Sporovibrio desulphuricans* to reduce sulphate under anaerobic conditions. The media were inoculated with *B. circulans* and *B. polymyxa* and incubated aerobically and anaerobically for 7 days at 30° and then tested for ferrous iron and growth noted. Good reduction and growth was obtained with both bacteria in the aerobic and anaerobic cultures growing on glucose and fructose. *B. circulans* showed very slight reduction under anaerobic conditions on peptone, asparagine, and citrate. *B. polymyxa* exhibited slight reduction under aerobic incubation on glycerol and lactate and under anaerobic conditions on peptone and citrate. Growth on all substrates except glucose and fructose was very slight or did not occur.

The Utilization of the Oxygen in Ferric Oxide

Leeper (1947) and Bétrémieux (1951) suggested that the oxygen of ferric oxide is utilized under anaerobic conditions by certain micro-organisms, and that as a result the iron becomes reduced.

Quastel *et al.* (1925) found that some bacteria could grow under anaerobic conditions on glycerol or lactate if nitrate was used as the nitrogen source, but not if ammonium nitrogen was used. The glycerol and lactate could not be oxidized to yield energy for growth in the absence of oxygen or a substance, such as nitrate, which could replace molecular oxygen.

It was reasoned that if the oxygen of ferric oxide could be used by iron-reducing bacteria then growth and reduction of iron should take place under anaerobic conditions in the presence of glycerol, ferric oxide, and ammonium nitrogen.

The following experiment was set up to study this aspect. Six media were prepared:

1. Medium *A*.
2. Medium *A* with 0·5 per cent. glycerol replacing sucrose.
3. Medium *A* with no carbon energy source.
4. Same as 1, but 0·1 per cent. $NaNO_3$ replacing $(NH_4)_2SO_4$.
5. ,, 2 ,, ,, ,, ,, ,,
6. ,, 3 ,, ,, ,, ,, ,,

The media were dispensed in 10 ml. lots in 6 in. $\times \frac{3}{4}$ in. test-tubes, and half received 1 ml. of hydrated ferric oxide suspension. The tubes were sterilized by autoclaving, inoculated with *B. polymyxa*, and incubated for 7 days at 30°, some aerobically and others anaerobically. The tubes were then examined for growth, ferrous iron, and reduction of nitrate, and the results are given in Table 2.

TABLE 2

Showing Growth, Reduction of Ferric Oxide and Nitrate by B. polymyxa *in Glycerol and Sucrose Media under Aerobic and Anaerobic Conditions after 7 Days at 30° C.*

	$(NH_4)_2SO_4$ *as N source*				$NaNO_3$ *as N source*					
	Growth		*Ferrous iron*		*Growth*		*Ferrous iron*		NO_3 *reduction*	
Medium	*aer.*	*an.*	*aer.*	*an.*	*aer.*	*an.*	*aer.*	*an.*	*aer.*	*an.*
Sucrose	++	++	..	..	+	+	..	..	+	+
Sucrose+$Fe(OH)_3$	++	++	++	++	+	+	++	++	+	+
Glycerol	+	−	..	..	+	+	..	..	+	+
Glycerol+$Fe(OH)_3$	+	−	+	−	+	+	++	++	+	+
No C source	−	−	..	..	−	−	..	..	−	−
No C source +$Fe(OH)_3$	−	−	−	−	−	−	−	−	−	−

Under aerobic conditions the bacterium grew in all media except the no carbon media and reduced nitrate and ferric oxide where present. At the time of testing neither nitrate nor nitrite could be demonstrated in

the cultures so presumably reduction had gone further than nitrite. Nitrite could be detected in 24-hour-old cultures. Under anaerobic conditions the two sucrose media enabled good growth and reduction of iron and nitrate to take place, but with the glycerol media growth and reduction occurred only in the glycerol nitrate medium. There was no growth or reduction under anaerobic incubation in the glycerol ammonium sulphate medium even when ferric oxide was present.

Reduction of Ferric Phosphate

The reduction of ferric phosphate and hydrated ferric oxide by *B. circulans* was tested in liquid medium *A* to see if another insoluble ferric compound could be reduced. The procedure was the same as that described earlier for testing iron reduction by various bacteria except that the tubes were incubated aerobically and anaerobically for 4 days. The results given in Table 3 show that the iron of both compounds was reduced.

TABLE 3

Showing the Reduction of Ferric Phosphate and Hydrated Ferric Oxide by Bacillus circulans *in Liquid Medium A after 4 Days at 30° C. under Aerobic and Anaerobic Incubation*

	Incubated aerobically		*Incubated anaerobically*	
Iron source	*pH*	*Ferrous iron in solution (mg./l.)*	*pH*	*Ferrous iron in solution (mg./l.)*
Ferric phosphate	5·5	25	5·5	40
Hydrated ferric oxide	5·6	16	5·6	40

The rust colour of the ferric oxide changed to a dark brown-black and the buff colour of the ferric phosphate to a grey-green during the course of incubation.

Determination of Soluble and Total Ferrous Iron in Cultures of B. circulans

To determine if all the ferrous iron in the cultures was in solution, tubes of medium *A* were inoculated, and some tubes received ferric oxide. The tubes were incubated aerobically and anaerobically, and after 5 days soluble ferrous iron was determined on 5-ml. samples of the supernatant in the cultures. Immediately after a sample had been taken, 5 drops of concentrated HCl were added to the rest of the culture and the culture shaken until all the $CaCO_3$ in the tube had dissolved. Ferrous iron was determined in 5 ml. of the acidified whole culture and the figure obtained was regarded as the total ferrous iron in the culture. To check against reduction of iron due to acidification, 5 drops of acid and 1 ml. of ferric oxide suspension were added together to cultures which did not receive ferric oxide initially. Ferrous iron was determined on samples of the resulting mixtures. Ferrous iron determinations were also made on

samples of the supernatant, which were treated with HCl before the addition of $\alpha\alpha'$ dipyridyl.

The determinations are given in Table 4.

TABLE 4

Showing Soluble and Total Ferrous Iron in 5-day-old Aerobic and Anaerobic Cultures of Bacillus circulans *grown in medium A*

	Ferrous iron determinations (mg./l.)*	
	Soluble	*Total*
Aerobic	110	160
Anaerobic	150	220
Acidified control + $Fe(OH)_3$.	0	8
Acidified supernatant (anaerobic)	145	..

* Average of 3 determinations.

There was a marked increase in ferrous iron after acidification of the deposit in the cultures which received ferric oxide at the time of inoculation, but only a slight reduction in the culture which received ferric oxide with the acid. There was no increase in ferrous iron when the supernatant was acidified.

The Effect of Aeration on the Reduction of Iron

To study the effect of various degrees of aeration on the reduction of iron by *B. circulans* in liquid medium *A*, the following experiment was made: 25 ml. aliquots of medium *A* were pipetted into 6 in. × 1 in. boiling-tubes and 50, 100, 250, and 500 ml. conical flasks. Each aliquot received approximately 0·01 g. ferric oxide and 1 drop of a suspension of *B. circulans*. Four of the boiling-tubes were incubated anaerobically and the remainder of the tubes and the flasks were incubated aerobically at 30° for 4 days. The degree of aeration was governed by the depth of medium and by the area exposed to air; thus aeration was related to area/depth, and using this as an index, the relative aerations of the media in the above vessels were 0·0, 0·3, 1·5, 10, 20, and 25 respectively. The depth of the cultures ranged from 0·4 to 2·5 in. and the area of the medium exposed to air, from 0 to 10 sq. in.

The pH of the undisturbed supernatants and of the cultures after shaking, and the total ferrous iron in the cultures were determined after 4 days. The results of these determinations appear in Table 5.

The total ferrous iron determinations do not give a complete indication of the amount of reduction which had taken place in the various cultures, because in some of the flasks, particularly the 50- and 100-ml. flasks, much of the ferrous iron became reoxidized to form a brown scum and deposit on the side of the flasks.

Following this experiment methylene blue was added to a 4-day-old aerobic culture of *B. circulans* in a 6 in. × 1 in. boiling-tube, and after

30 minutes the methylene blue was completely decolorized except at the surface and along convection currents.

TABLE 5

Showing the Effect of Degrees of Aeration on the Reduction of Iron by Bacillus circulans *after 4 Days at 30° C.*

Vessel containing culture	*Aeration index: surface area of culture / depth of culture*	*pH*		*Total ferrous iron (mg./l.)*
		Supernatant	*Suspension*	
6″ × 1″ boiling-tubes (anaerobic)	0	5·6	6·5	120
6″ × 1″ boiling-tubes (aerobic)	0·3	5·6	6·5	60
50-ml. conical flask	1·5	5·8	6·3	28
100-ml. conical flask	10	5·7	6·3	26
250-ml. conical flask	20	5·9	6·5	22
500-ml. conical flask	25	6·5	6·8	13

Discussion

This study has shown that the reduction of iron compounds is not caused only by *Bacillus polymyxa* as suggested by Roberts (1947) but that at least one other different species, *Bacillus circulans*, can reduce iron extensively; other bacteria of the genera *Escherichia* and *Aerobacter* are also able to do this to a limited extent in certain media. An examination of more species of *Bacillus* may reveal others that can reduce iron. The reduction of iron by bacteria in some media and not in others raises the question as to what medium is best suited for the study of iron reduction as it occurs in soil. As Bloomfield (1950) pointed out, the use of media in which the pH falls to values below 5 during growth are to be avoided, as these values are lower than those usually found in gleyed soils. Medium *A* seemed better than those used by Halvorson and Starkey (1927) or Roberts (1947), since in this medium the pH did not fall below pH 5·5 and yet extensive iron reduction occurred. When Difco yeast extract was omitted from medium *A* some of the bacteria which could reduce iron failed to grow. If, however, the deficient medium was inoculated with a mixture of *B. circulans* and a soil bacterium (*Achromobacter* sp.) which could grow but not reduce iron in the unenriched medium, the *B. circulans* was able to develop and extensively reduce iron. The *Achromobacter* sp. presumably synthesized some substance which enabled the growth of *B. circulans* (Lochhead and Chase, 1942).

The absence of iron reduction in dilutions of gleyed clay from 10 ft. indicates that the gleying at this depth is not due to the activities of the bacteria which develop in medium *A* but is due to other types of bacteria or more probably due to organic substances, similar to those suggested by Bloomfield (1951), which can dissolve and reduce ferric compounds. The presence of iron-reducing organisms in samples from 2 ft. makes it possible that in the shallower layers of soils, where there is organic matter available to micro-organisms, the micro-organisms supplement the

gleying action of plant-reducing substances. *B. circulans* and *B. polymyxa* did not grow or reduce iron anaerobically in the presence of a number of oxidizable substrates, and further, *B. polymyxa* did not grow or reduce iron in the presence of glycerol under anaerobic conditions unless nitrate was present. These results suggest that the reduction of iron is not directly involved in the oxidation of the substrate as is the case when sulphate and nitrate are reduced. It would appear that the iron is reduced irrespective of whether it is an oxide or another insoluble ferric compound and that not all the ferrous iron is in solution. The formation of acids in the culture probably favours the solution of ferrous iron.

The aeration study indicates that the reduction of iron can occur in quite shallow cultures which have a large surface exposed to air, but that as the degree of aeration increases the actual amount of ferrous iron in the culture decreases to quite a low level. The experiment with methylene blue indicates that although the cultures are exposed to air, the bottom of the tube where the iron is is anaerobic. It is suggested that in soil which appears to be aerobic there are localized sites near available organic matter which are anaerobic and that reduction of iron can take place in these zones. Preliminary experiments show that oxides of manganese behave in a similar way to iron.

Summary

Bacteria that could reduce ferric compounds in various media were isolated from soil and grass and were identified. Their activity differed greatly, and the most active species, *Bacillus circulans* and *Bacillus polymyxa*, isolated from soil were selected for further study.

Growing cultures of the organisms reduced ferric compounds in liquid media kept under anaerobic conditions, with the formation of soluble and insoluble ferrous compounds. Reduction of ferric hydroxide also occurred in liquid cultures exposed to air, but here the amount of ferrous iron decreased as the surface area was increased.

These organisms were unable to derive oxygen for their growth from ferric oxide under anaerobic conditions, but where another compound containing available oxygen was supplied, growth, and reduction of ferric compounds, occurred.

Iron-reducing bacteria were found in the surface layers of gleyed soil, but not in samples taken at a depth of 10 ft.

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*A MINERALOGICAL STUDY OF THE COLLOID FRACTIONS OF SOME GREAT SOIL GROUPS, WITH PARTICULAR REFERENCE TO ILLITES

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Introduction

LITERATURE on clay minerals, their nature and profile distribution, particularly on a horizon basis with respect to different great soil groups, is very scanty.

From the works of Jacob *et al.* (1935), Nagelschmidt *et al.* (1940), Kelly *et al.* (1939), Alexander *et al.* (1939), Russell and Haddock (1940), and Coleman and Jackson (1945) it seems that (1) highly leached soils such as podzols and laterites tend to present kaolinitic clays; (2) with very few exceptions the clay fractions are composed of two or three types of minerals; but information on the relative proportion of the constituent minerals in the clay fractions of different horizons of different soil groups does not appear to be available.

The present investigation was undertaken to study the nature, profile distribution, and relative proportion of the clay minerals with respect to natural horizons of some Australian major soil groups such as red-brown earths, solodized-solonetz, solod, and rendzina.

Experimental and Discussion

Clay fractions separated from the soil samples taken from the different horizons of the soil groups under investigation were X-rayed, and the crystallographic analyses revealed that:

(i) except in the rendzina soils the clay minerals were present as combinations of illite and kaolin in varying relative proportions with minor associations of quartz and/or goethite generally in the A_2 horizon;

(ii) in the rendzina soils the clay fractions were mainly illitic with a kaolin content < 10 per cent., and hence the clay samples might be regarded as rather pure specimens of illite, due allowance being made for the pedogenic origin;

(iii) in the red-brown earths, solodized-solonetz, and solod soils which exhibited distinct podzolic nature (Karim, 1951, 1953), the illite: kaolin ratio showed distinct decrease with depth, especially in the solod which exhibited relatively the highest podzolic nature, and wherein the illite:kaolin ratio was 50:50, 40:60, 30:70 in the A_2, B_1, and B_2 horizons respectively, the decrease of the ratio also appeared to bear a direct relationship with the degree of podzolic activity;

* Based on a portion of a Ph.D. Thesis, Adelaide University, 1951.

(iv) the decrease of the ratio with podzolic activity and with depth under podzolic influence was due to higher kaolinization accompanied by a corresponding lowering of the illite content as though the kaolinization was taking place at the expense of illite.

Study of the Illites

The term 'illite' was introduced by Grim, Bray, and Bradley (1937) who assigned (1) a SiO_2/R_2O_3 ratio of 3, (2) a K_2O content of 6–7 per cent. as a critical value, (3) a cation-exchange capacity of 20–40 m.e. per cent. to the mineral. Endell *et al.* (1935), however, suggested a cation-exchange capacity of 50 m.e. per cent. for *Glimmerton* which was accepted by Grim *et al.* (loc. cit.) to be similar to illite.

But the above reports on illites were all pertinent to those isolated from native rocks, and information on this mineral found in the clay fractions of natural soil horizons is unavailable.

It was thus felt desirable to study the illites for their chemical composition and cation-exchange capacity (hereinafter referred to as 'capacity') to see how they compare with those of Grim *et al.*

(A) *The* SiO_2/R_2O_3 *ratio and capacity*

The clay fractions of the rendzina soils were suitable for this purpose as they were found to present reasonably good specimens of illite, as discussed previously.

The capacity of the mineral fraction was computed from the regression equation: $y-\bar{y} = b_1(x_1-\bar{x}_1)+b_2(x_2-\bar{x}_2)$, where y, x_1, x_2, b_1, b_2, $\bar{y}$, $\bar{x}_1$, and $\bar{x}_2$ represented respectively the capacity in m.e. per cent. of the whole soil sample, per cent. clay, per cent. organic carbon (as a measure of organic colloid), capacity due to clay, capacity due to organic colloid, mean y, mean x_1, and mean x_2.

The gram-molar SiO_2/R_2O_3 ratios of the clay separates were also determined.

Discussion. The results of the analyses as presented in Table 1 reveal that (1) the SiO_2/R_2O_3 ratio of the clay fractions showed a value of 3–3·15, thereby agreeing quite well with that of Grim *et al.*; (2) the capacity of the clay fraction under the investigation was 52 m.e. per cent., which seems to merit a further discussion.

The deduction of the capacity of the clay mineral from that of the whole soil sample is difficult due to the facts that: (*a*) the clay fraction contained also about 10 per cent. of kaolin which lowered the capacity accordingly; (*b*) according to Kelly (1948) the coarser fractions—silt and fine sand—also possess cation-exchange power which implies that the calculated capacity in the present investigation is a bit higher than the actual capacity of the clay as the contribution due to the coarser fractions towards the capacity of the soil has been included in the share of the clay fraction and the organic-colloid fraction during the calculation.

Assuming the capacity of the illites under investigation to be 50 m.e. per cent., the presence of about 10 per cent. kaolin in the clay fraction would reduce the value to 46 m.e. per cent. to the lowest, and the coarser fractions would account for 52−46, i.e. 6 m.e. per cent.—but this again

is an assumption. If not, the alternative would be 40 m.e. per cent.—the maximum value due to Grim *et al.* If so, the coarser fractions will have to stand for the reduction due to the kaolin (52—37) m.e. per cent., i.e. a capacity of 15 m.e. per cent. Again, the coarser fractions as discussed under (*b*) above had to have contributed a part of their capacity to the organic matter too, which certainly implies that the coarser fractions must have had a capacity $>$ 15 m.e. per cent.—an idea very difficult to see, at least in the absence of any experimental evidence.

TABLE 1

$SiO_2:R_2O_3$ *Ratio and Cation-Exchange Capacity of the Illites Studied*

Soil type	*Depth in inches*	*Clay minerals*	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$*	*Cation-exch. cap. in m.e. % of the soil*	*% clay*	*% org. carbon*
Rendzina (A)	0–7	Mainly illite and a little kaolin (10%)	3·05	38·77	41·4	1·53
	9½–15½	,,	3·00	31·02	38·0	0·68
	20–29	,,	3·15	29·91	37·2	0·33
	38–60	,,	3·10	20·03	21·8	0·17
Rendzina (B)	0–3½	,,	3·02	39·29	39·9	1·62
	3½–6½	,,	3·10	39·36	41·6	1·33
	7½–14	,,	3·15	41·70	49·6	0·81
	15–28	,,	3·16	27·95	33·2	0·35
	35–50	,,	3·07	20·61	25·1	0·13

* On ignited clay.

It thus seems desirable to assign a value of 50 m.e. per cent. as the capacity of the illites under investigation, thereby supporting the findings of Endell *et al.*

(B) *The* K_2O *and* MgO *content of the illites*

As the K_2O content of illites has been shown to be quite a critical and reliable index, an examination of the K_2O and also MgO contents of the illites under investigation was undertaken.

The clay separates were selected so that they were composed of illite and kaolin only with a sequence of relative proportions of illite to kaolin (viz. I:K = 30:70, 40:60, 50:50, 60:40, and 70:30).

Discussion. The results of the analyses as presented in Table 2 show that

(i) the percentages of K_2O computed on 100 per cent. illite basis varied around 6·4, which is just about the same value as reported by Grim *et al.*;

(ii) the MgO contents did not agree with those of Grim *et al.*, who reported a value of 2·7 to 3·9 per cent., probably because of the isomorphous substitutions taking place in the octahedral position during pedogenesis. It would perhaps be too much to expect the MgO content of native-rock illites to be the same as that of illites occurring in soil-horizon clays.

The interpretations of the results of the whole investigation were based on the assumption that the quantitative aspect of the X-ray

TABLE 2

*K_2O *and* MgO *Contents of Illites*

Clay separate	*Minerals present*	% K_2O *in the combination*	% MgO *in the combination*	% K_2O *in 100% illite*	% MgO *in 100% illite*
A	Illite : Kaolin (70 : 30)	4·54	1·41	6·48	2·01
B	Illite : Kaolin (60 : 40)	3·67	1·22	6·11	2·03
C	Illite : Kaolin (50 : 50) Quartz—20%	2·56	0·49	6·40	1·22
D	Illite : Kaolin (40 : 60)	2·55	0·61	6·37	1·52
E	Illite : Kaolin (30 : 70)	1·98	0·45	6·60	1·50

* Expressed on ignited clay.

analyses was true. As a test of this the K_2O contents of the clay samples were plotted against the respective illite contents and the curve obtained (Fig. 1) was nearly linear, thereby indicating the validity of the above assumption.

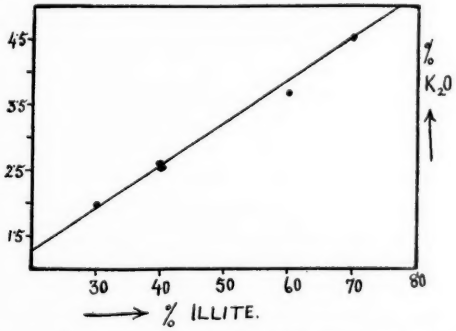

FIG. 1. Illustrating the relationship between the K_2O content and illite content in selected clay samples.

Analytical methods. The methods employed were those described by Piper (1947).

Summary

The investigation deals with a study of the minerals present in the clay fractions of the natural horizons of some major groups of soils of Australia.

The results of the investigation may be summed up as follows:

(i) the clay fractions were composed mainly of illite and kaolin in varying relative proportions with occasional minor associations of quartz, goethite, &c.;

(ii) the rendzina-soil clays were rather pure specimens of illite (the kaolin content being < 10 per cent.) with no variation with depth;

(iii) the advance of podzolic activity was followed by an increase of kaolin content with a corresponding decrease of the illite content in the clays—remarkably so with reference to vertical distribution, i.e. the more the podzolic activity the more was the illite : kaolin ratio narrowed irrespective of group, type, or depth;

(iv) the chemical composition of the illites showed good agreement with that suggested by Grim *et al.*, excepting the MgO content;

(v) the cation-exchange capacity of the illites indicated a value of 50 m.e. per cent., thereby showing similarity to the *Glimmerton* of Endell *et al.* (1935).

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SOIL MORPHOLOGY AND MINERALOGY. A QUALITATIVE STUDY OF SOME GLEYED SOILS FROM NORTH-WEST ENGLAND

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It has been pointed out (Brown, 1953*a*) that previous mineralogical studies of soils have only dealt with the minerals present in the different soil horizons *in toto* and suggested that more could be found out about soil formation by studying the connexion between the detailed morphology of a soil and its mineralogy. In addition to information on soil formation, any widespread application of clay mineralogy to agriculture will only be possible by using soil maps which are based on morphology. The present study is an attempt to relate morphology to mineralogy. The experimental work reported in this paper was done before the micro-technique described previously (Brown, 1953*a*) had been fully worked out, so instead of investigating discrete mottles, groups of mottles from the soil horizons were studied.

The soils investigated belong to the gley group, and in those horizons where the mottling was strong it was possible to separate the orange or brown mottles from the associated grey material by hand-picking. In this way two samples were obtained from each mottled horizon, a brown sample and a grey sample. It has been shown by X-ray diffraction studies that the clays from associated brown and grey separates differ only in the quantity of iron oxides they contain. The brown separates all contain lepidocrocite and some contain goethite as well. The grey clays contain neither. The alumino-silicate clay minerals in brown and grey samples from the same horizon are very similar, but they vary from one horizon to another.

Soils

The three soils, MCF 1, MCF 2, and MCF 3, occur close to each other at Moses Cocker's Farm, Rivington, Lancashire. They are formed on similar parent materials and differ chiefly in degree of gleying, MCF 1 being slightly gleyed, MCF 2 moderately gleyed, and MCF 3 strongly gleyed. Profile descriptions by Mr. E. Crompton are given in the appendix. The brown and grey soil separates from which the clays were obtained were those separated and analysed by Bloomfield (1952*a*). These were MCF 1, 24–27 in.; MCF 2, 10–13 in. and 32–36 in.; MCF 3, 1½–10 in., 14–25 in., 25–30 in., 30–37 in. The soils were dispersed in water using Calgon (sodium hexametaphosphate). No other pre-treatment was needed either to disperse the clays or to obtain good clear X-ray diffraction patterns. There was less than 1 g. of each separate available, so pipette samples were taken from the soil dispersions at 2 cm. depth after they had been left to settle for 3 hours and 12 minutes at 20° C. This gives clay e.s.d. $< 1{\cdot}4\ \mu$. Oriented aggregates of the fourteen clays were made by the centrifuge method (Brown,

1953*a*), and air-dry oriented aggregates were photographed with CoK_α radiation.

Distribution of Iron Oxides in the Clays

The brown separates from the soils all contain hydrated ferric oxides while the grey separates do not. Lepidocrocite, γ-$Fe_2O_3.H_2O$, is present in all the brown separates and goethite, α-$Fe_2O_3.H_2O$, is present in some. Table 1 shows their distribution in the brown separates. A notable feature is that in MCF 2, 10–13 in., where the lepidocrocite pattern is weak, the goethite pattern is strong. The impression given by the photographs of MCF 3 profile is that the amount of lepidocrocite in the brown separates increases downwards, but quantitative estimates of the amount of these oxides in the mottles would not add to our knowledge as their proportions would depend on the efficiency of separation of the brown mottles from their surrounds.

TABLE 1

Soil	*Indications of lepidocrocite*	*Indications of goethite*
MCF 1, 24–27 in.	Present; strong pattern	Absent
MCF 2, 10–13 in.	Present; weak pattern	Present; moderately strong pattern
32–36 in.	Present; strong pattern	Present; weak pattern
MCF 3, 1½–10 in.	Present; strong pattern	Present; very weak pattern
14–25 in.	Present; strong pattern	Absent
25–30 in.	Present; strong pattern	Absent
30–37 in.	Present; strong pattern	Absent

The Alumino-silicate Minerals

Identification

Patterns of air-dry oriented aggregates have lines at 7·1 Å, 10 Å, and 14 Å, with their lower orders; the main differences between different samples are in the relative intensities of these reflections. None of the patterns is changed by prolonged glycerol treatment of the specimen so montmorillonoids, as usually defined, are not present. Taking the reflections in turn the 7·1 Å reflection is (001) of a kaolin mineral and/or the second-order basal reflection of the 14 Å mineral. The 10 Å line can be attributed to a hydrous mica and the 14 Å line is caused by either chlorite or vermiculite or both. Heating to 600° C. for half an hour collapses vermiculite to a 10 Å spacing (Walker, 1949*a*), while the 14 Å reflection of chlorite does not shift and is enhanced in intensity (Brindley and Ali, 1950). This test was carried out and showed that chlorite was present only in the deepest horizons and in very small amounts. Higher up the soil profile there is no 14 Å line after heating to 600° C., although even in the surface soil a very weak 3·5 Å line persists which is either the fourth order of a 14 Å line or more probably the strongest reflection of anatase. A kaolin mineral is shown to be present by heating the clay from the surface soil to 400° C. for several hours, immediately sealing the clay from the air, and photographing. This photograph shows that the 14 Å spacing of the vermiculitic component

has collapsed to 10 Å and a strong 7·1 Å line, due to the kaolin mineral, persists. The vermiculitic mineral differs from true vermiculite in several respects, and although a full discussion is not appropriate here, a summary of its investigation is given.

MCF 2 soil was used for detailed investigation of the 14 Å mineral. It is not yet possible to separate the components from mixtures of soil clays, so interpretation is often complicated. Walker (1949*a*) said that the 14 Å vermiculite reflection shifts to about 11 Å when the clay is boiled for 5 minutes with $[NH_4]^+$ solutions, but in the MCF soils the 14 Å line was unaffected by 10 minutes' boiling in a large excess of N-NH_4NO_3. However, boiling for 8 hours in excess NH_4NO_3 gave an appreciable increase in the intensity of the 10 Å line, although the 14 Å line was still quite strong. After boiling the clay in KOH+KCl for several hours the 14 Å line disappeared and was replaced by a 10 Å line which had a slight tail on the low angle side. This K^+ treated clay, when boiled with $MgCl_2$ solution, gives a clay which as far as interlayer expanding properties are concerned behaves like normal vermiculite. Treatment of the soil clay with hydrogen peroxide gave a clay in which the 14 Å mineral reacted with $[NH_4]^+$ solutions more quickly than untreated clay but not as quickly as normal vermiculite. These experiments suggest that the mineral differs from vermiculite in having an exchangeable cation which is very difficult to replace. That hydrogen peroxide speeded its rate of reaction with $[NH_4]^+$ ions and that KOH treatment allowed it to react with potassium ions suggest that organic compounds, either by retention as exchangeable ions or by physical blocking, are responsible for this difference from true vermiculite. Bloomfield (1952*b*) has shown that plant extracts can mobilize iron as ferrous-organic complexes in soils, and Schnitzer and DeLong (1952) have said that these complexes are ionic. Thus it is possible that the ferrous-organic or perhaps alumino-organic complex ions are sorbed by the vermiculitic mineral as exchangeable cations. Another possibility is that $[Al(OH)_2]^+$ or $[Al(OH)]^{2+}$ ions or more complex $[Al_m(OH)_n]^{(3m-n)+}$ ions are present in the interlayer positions. These might be removed by KOH. The effect of peroxide in making them more readily removable might be that the mineral is exfoliated by peroxide and hence these ions are made more readily accessible for exchange. It will not be easy to find the real explanation as the complication of organic matter added to the fact that the soil clay is a mixture of minerals means that chemical data would be even more difficult to interpret than X-ray diffraction patterns.

Powder photographs, using sodium chloride as an internal standard, show that the 14 Å mineral has an (060) spacing of 1·500 Å. This suggests that the mineral is dioctahedral (Walker, 1949*b*, 1950). Thus the 14 Å mineral seems to be the dioctahedral analogue of vermiculite and the slower reaction of the untreated soil clay with ammonium ions is probably caused by the kind of exchangeable cation present. The hydrous mica in the lower layer also has an (060) spacing of 1·500 Å. In fact, all the powder patterns of this profile show only two (060) lines, that of the kaolin mineral at 1·488 Å and that of the mica or vermiculitic member at 1·500 Å.

Profile relations

It will remain generally impossible to make quantitative determinations of clay minerals until much more is known about them. Differences in diffraction effects between standard minerals and those present in the unknown can cause serious errors, for large differences in intensities can be caused by isomorphous replacements (Brown, 1951 and unpublished). However, questions that can be answered about the clay minerals in these soil profiles are:

(*a*) Are the clay minerals in the brown separates identical with those in the grey separates from the same soil horizon?
(*b*) What trends are shown by the intensity variations from horizon to horizon?

In the absence of quantitative data, the only way to compare the clay mineral variation between samples is to study the change in the intensity ratios, $I_{7\cdot1}/I_{6\cdot25}$, $I_{7\cdot1}/I_{10}$, I_{10}/I_{14}, and $I_{7\cdot1}/I_{14}$.

Intensity Measurements

To obtain the intensity ratios, photometric measurements were made of the X-ray patterns, using a recording microphotometer. To find how and why the photometric intensity measurements vary the following tests were made.

1. Two photometer traces were made of an oriented aggregate photograph of one of the brown clays without moving the film on the photometer film carrier between traces. In this way, exactly the same part of the film was measured each time. This tests the variability of the instrument. There was only about 1 per cent. difference in $I_{7\cdot1}/I_{6\cdot25}$ between the two traces.

2. As test 1, but the film was removed and then replaced as near as possible to its previous position on the film carrier between traces. $I_{7\cdot1}/I_{6\cdot25}$ varied by almost 10 per cent. in this test. If the film is not replaced on the film carrier exactly as before between traces, the effect of grain in the film would be introduced and this might explain the variation.

3. Two traces were made of two different photographs of the same flake specimen, the orientation of the flake to the incident X-ray beam being unchanged between photographs. This tests the reproducibility of the photographic procedure. Once again the variation in $I_{7\cdot1}/I_{6\cdot25}$, about 10 per cent., can be attributed to the grain of the film.

4. As in 3 above, except that the flake specimen was reset with respect to the incident X-ray beam between photographs. This tests the ability of the operator to orient the specimen in the X-ray camera as the setting is done by eye. Variation in $I_{7\cdot1}/I_{6\cdot25}$ is again about 10 per cent.

5. Traces were made of photographs of two different flake specimens of similar width cut from the same clay aggregate to test constancy of composition of the clay aggregates. Variability is about 10 per cent.

6. Traces were made of photographs of two different flake specimens of very different width cut from the same clay aggregate to test the

absorption effects in the flake. The variation in the ratio is again about 10 per cent.

The 10 per cent. variation in tests 2, 3, 4, 5, and 6 is probably caused by grain in the film. Test 6 is a favourable case for reproducibility since the two reflections being compared occur at close θ values. The variation in intensity ratios would probably be greater with specimens of very different width if lines of more widely differing θ's were used for comparison. However, in practice it is easy to keep specimen width nearly constant.

As already mentioned, air-dry oriented aggregate patterns of the MCF clays have lines at 7·1 Å, 10 Å, and 14 Å, but intensity distribution between them varies from horizon to horizon. On all the patterns there is some diffuse scattering between the 10 Å and 14 Å lines and also some continuous scattering extending from 24 to 28 Å upwards. Diffuse scattering was ignored in making intensity measurements; peak intensities only were measured, there being no easy way to measure the magnitude of diffuse scattering.

The intensity ratios could vary from sample to sample for two reasons:

1. If the different mineral groups are identical, each to each, in chemical composition and in structure in the samples being compared, different amounts of each group would cause the intensity ratios to vary from sample to sample.
2. If the amounts of each mineral group are constant from one sample to another, variations in chemical composition by isomorphous replacement could give wide intensity variations.

If the intensity ratios are constant, or nearly so, between any two samples, either the minerals present are similar in kind and amount, or (1) and (2) above have varied reciprocally. If the ratios are close the mineral composition of the two samples is probably the same.

Table 2 gives a comparison of the intensity of associated brown and grey clays.

The similarity of the ratios in Table 2 suggests that the clay minerals of the brown and grey separates of any single horizon are identical in kind and amount.

Some of the ratios in Table 2 show a greater variation than the 10 per cent. found in the photometer tests, and possible sources of error in this table and Table 3 are:

1. Difference in clay sampling between samples. When taking samples from 2 cm. depth a small error in depth could give quite a wide variation in particle size distribution in the clay.
2. Instead of printing a calibration strip on each film to relate X-ray intensity to optical density, the average curve for four films was used for all. Deviations of a particular film from the average would cause errors.
3. On some films the four lines, i.e. 6·25, 7·1, 10, and 14 Å, have a wide range of intensity. Thus sometimes the intensity of very weak lines has to be measured, and this is difficult to do accurately.

TABLE 2

Soil . .	*MCF 1*		*MCF 2*						*MCF 3*					
Depth . .	*24–27 in.*		*10–13 in.*		*32–36 in.*		*1½–10 in.*		*14–25 in.*		*25–30 in.*		*30–37 in.*	
	Brown	*Grey*	*Brown*	*Grey*	*Brown*	*Grey*	*Brown*	*Grey*	*Brown*	*Grey*	*Brown*	*Grey*	*Brown*	*Grey*
Intensity ratios														
$I_{7\cdot1}/I_{6\cdot25}$	1·56	..	3·94	..	0·89	..	0·59	..	0·42	..	0·29	..	0·20	..
$I_{7\cdot1}/I_{10}$	2·44	2·76	2·07	2·34	0·80	0·72	1·13	1·46	1·05	0·84	0·95	0·82	0·70	0·80
I_{10}/I_{14}	1·59	1·38	0·60	0·61	2·56	2·72	0·33	0·27	1·42	1·65	1·58	1·76	2·35	2·48
$I_{7\cdot1}/I_{14}$	3·88	3·81	1·24	1·42	2·05	1·96	0·37	0·40	1·49	1·39	1·50	1·44	1·66	1·99

TABLE 3

Soil . .	*MCF 1*	*MCF 2*		*MCF 3*			
Depth . .	*24–27 in.*	*10–13 in.*	*32–36 in.*	*1½–14 in.*	*14–25 in.*	*25–30 in.*	*30–37 in.*
Intensity ratios							
$I_{7\cdot1}/I_{10}$	2·60	2·22	0·76	1·30	0·95	0·89	0·75
I_{10}/I_{14}	1·49	0·61	2·64	0·30	1·54	1·67	2·42
$I_{7\cdot1}/I_{14}$	3·85	1·33	2·01	0·39	1·44	1·47	1·83

4. Incoherent background scattering increases rapidly from about 7 Å to the primary beam on these films and as the 10 and 14 Å lines are not sharp and well resolved, it is difficult to estimate their background accurately. Fig. 1 shows a photometer trace of MCF 2, 32–36 in. (brown separate) which illustrates this difficulty.

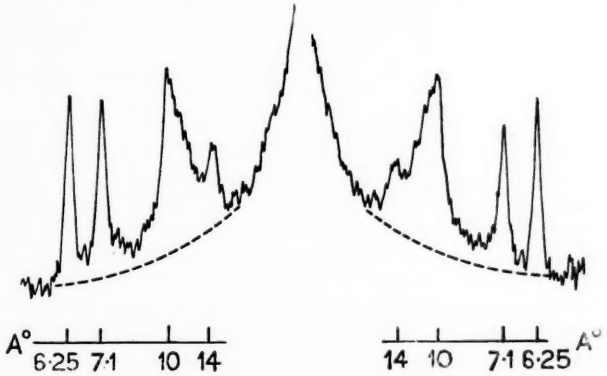

FIG. 1. Photometer trace of MCF 2, 32–36 in. (brown separate). This shows the trace on either side of the primary beam. The background is sketched in as a dotted line but it will be seen that different curvatures could be given to this line which would affect the measured intensities.

Table 3 gives the changes in intensity ratios of the clay minerals through the soil profile, the mean values from Table 2 being used.

Discussion

Table 2 shows that the only difference between the brown and grey clays is their iron oxide content; the alumino-silicate clay minerals in any pair of samples are identical in kind and amount. If clay minerals are taken as criteria of alteration or weathering, then the grey and brown patches are equally altered. This similarity also shows that the same process of clay mineral formation goes on in both brown and grey materials at a particular depth. If, as seems likely, the iron content was spread evenly through the original ground mass, then the iron oxides in the soil formed either at the same time as or after the clay minerals were formed.

Since the alumino-silicate fractions of the grey and associated brown clays are identical, we are led to a method for the quantitative estimation of the crystalline iron oxides in the brown clays and in the whole soil. For this, mixtures of the pure oxide and the appropriate grey clay can be used as standards. The method of standard mixtures, which is inapplicable to clay minerals in general, can be used for the hydrated ferric oxides as there is no record of important isomorphous substitution in either lepidocrocite or goethite; therefore mineral lepidocrocite or goethite of the same particle size as the soil clay should give identical

diffraction effects to the iron oxides in the soil clay. We have, thus, a three-component system—lepidocrocite, goethite, and alumino-silicate minerals. The pure alumino-silicate component is obtained from the grey separate, as it is shown in Table 2 that its diffraction effects are identical to those of the alumino-silicate component in the associated brown clay. Thus a major difficulty of quantitative estimations of soil clays, that of obtaining the components in a pure state, has already been overcome by the soil-forming processes. It should be noted that the quantitative estimation of the individual alumino-silicate clay minerals is still impossible.

Previous observations (Brown, 1953*b*) and the evidence here shows that lepidocrocite is the main pigment in the mottles in gley soils. Goethite, when present, occurs in greatest amount near the surface. This suggests that rate of oxidation of ferrous compounds controls whether lepidocrocite or goethite is formed, as in poorly drained soils the rate of oxidation will generally be greater near the surface. Further evidence in favour of this hypothesis is that there is more goethite in MCF 2 than in MCF 3 and MCF 2 is better drained and so better aerated than MCF 3. On this hypothesis we might expect to find goethite in MCF 1, 24–27 in., but there is no evidence for it there.

Walker (1949*b*, 1950) has shown that in north-east Scotland biotite alters to vermiculite in soils. In the clay fraction of the MCF soils the dioctahedral mica of the lower layers is largely replaced by what appears to be the dioctahedral analogue of vermiculite in the surface. To go from a mica structure to a vermiculitic structure requires a decrease in the negative charge on the alumino-silicate layers. In the change biotite to vermiculite this might be brought about by the oxidation of ferrous iron, but with dioctahedral micas, which are usually mainly aluminous, this change is not possible to any large extent. Of course, there need be no direct relation between the two clay fractions and the clay of the upper horizons may be formed from the products of solution not only of clay but also of the coarser silt and sand fractions.

As regards amounts of minerals in the various horizons of MCF 3, no precise estimate of the amount of kaolin can be given, although it occurs in moderate amount throughout the profile as judged from photographs of the clays heated to 400° C. Table 2 shows that the mica dominates the remainder of the clay fraction in the lowest layer of the profile and the vermiculitic mineral predominates in the surface. The intermediate layers have intermediate amounts. The ratio I_{10}/I_{14} for MCF 3 shows only a slow decrease until the 1½–10 in. layer is reached. The sudden increase in the ratio $I_{7\cdot1}/I_{10}$ here could be accounted for by a decrease in the amount of mica and hence of the intensity of the 10 Å line without any increase in the amount of kaolin. In addition to this decrease, although the second-order basal reflection of the vermiculitic mineral is probably weak it may contribute to the intensity of the 7 Å line. The simplest explanation of the MCF 3 intensity ratios in Table 3 is that there is a decrease in the amount of the 10 Å mineral, i.e. mica from the bottom of the profile upwards, an increase in the amount of the 14 Å, i.e. vermiculitic mineral from the bottom of the profile upwards,

and that amount of the kaolin remains fairly constant throughout the profile. This deduction relies on the assumption that in the soil the vermiculitic mineral, the mica, and the kaolin in any one horizon is chemically identical with the corresponding mineral in the other horizons, i.e. changes in X-ray intensity ratios through the soil profile are caused solely by changes in relative amounts of minerals rather than by changes in diffraction effects due to such changes as isomorphous replacements.

Conclusions

1. Hydrated ferric oxides are the pigments of the mottles in gley soils, lepidocrocite being present in the brown or orange mottles of all the soils studied, and goethite in some. It is suggested that rate of oxidation decides whether lepidocrocite or goethite is formed, slow oxidation favouring the formation of lepidocrocite.

2. The only difference between associated brown and grey clays is their iron-oxide content; the alumino-silicate clay minerals in any pair of samples seem to be identical in kind and relative amount.

3. Kaolin is present in moderate amount throughout the profiles. What appears to be a dioctahedral vermiculitic mineral gradually replaces a dioctahedral hydrous mica, the chief clay component in the lower layers, until it becomes the dominant clay mineral near the surface.

4. The dioctahedral vermiculitic mineral has a slow rate of cation exchange judged from its rate of reaction with ammonium ions. This is probably due to the difficulty of replacement of the cations present in the natural condition.

5. The approach to pedogenesis used in this work, viz. relating morphology to mineralogy, promises to give useful results. Even more valuable would be the precise correlation of mineralogy and chemistry with detailed field morphology.

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APPENDIX

This appendix gives brief profile descriptions by Mr. E. Crompton of the soils from Moses Cocker's Farm which were used in this work.

Profile Descriptions

MCF 1. *Locality*: Moses Cocker's Farm, Rivington, Lancs. *Series*: Charnock. *Drainage of profile*: Imperfect. *Drainage of site*: Satisfactory. *Parent material*: Till of Carboniferous material. *Vegetation*: Agrostis, rye grass, and white clover.

Profile

0–3 in.	Very dark brownish-grey (10 YR 3/1), tight root mull, organic silt loam, well-developed fine crumb to fine granular structure, moist. Clearly defined boundary.
3–12 in.	Greyish-brown (9 YR 4/2), medium loam, very fine blocky to sub-angular blocky structure; numerous roots and root tracks penetrating down from above. Merging boundary.
12–22 in.	Yellowish-brown (9 YR 5/6), with some very pale grey, rather diffused and poorly defined mottling, fine sandy clay loam; structure is weakly developed but breaks easily to fine crumb; porous and fissured with some darker old worm tracks penetrating from the horizon above. Merging boundary.
22 in.+	Dull brown (10 YR 4/2), pale grey (2·5 Y 6·5/2) and ochreous on old root channels (5 YR 5/8) with some darker patches (probably MnO_2) fine sandy clay loam with some fine sandstone fragments tending to be laminated, probably reflecting the bedding of the parent material.

MCF 2. *Locality*: Moses Cocker's Farm, Rivington, Lancs. *Series*: Hallsworth. *Drainage of profile*: Poor. *Drainage of site*: Satisfactory. *Parent material*: Till of Carboniferous material. *Vegetation*: *Nardus*, *Deschampsia*, *Juncus*.

Profile

2–0 in.	Peaty mat. Sharp boundary.
0–2 in.	Dull darkish-grey (10 YR 3/1), with fine rusty mottling peaty loam; tendency to small prismatic structure; slightly porous and fissured; friable; much organic matter; some iron-oxide staining on roots and structure faces; passing clearly but irregularly into
2–5 in.	Dull grey (2·5 Y 4/2) with very much rusty mottling (2·5 YR 2/4) on structure faces and root channels, clay loam; very fine cloddy structure; much iron-oxide staining on root channels and structure faces merging into
5–9 in.	Dull grey (2·5 Y 4/2), with very little mottling on roots, clay; some iron-oxide staining on pebbles, root channels; passing clearly into
9–14 in.	Mainly pale grey (2·5 Y 6·5/2), with fair amount of fine orange and yellow spotting increasing downwards, clay; fissured tough plastic; some small black pellets (MnO_2?); merging into
14–24 in.	Orange (7·5 YR 5/8) and pale grey (5 Y 6/1·5) along root channels and structure faces in about equal amounts, clay; very strong prismatic, fissured, merging into
24–36 in.	Brighter and more orange (7·5 YR 5/8) with pale grey (5 Y 6·5/1) on structure faces and root channels, slightly gritty clay; rather weaker prismatic structure, fissured; merging into
36–48 in.	Basic colour—dull olive-brown (2·5 Y 4·5/4) but much orange (7·5 YR 5/8) and pale grey (4 Y 6/1) on root channels, gritty sandy clay; weaker cloddy structure slightly porous and fissured; merging into
48 in.+	Olive-brown (2·5 Y 4·5/4) with some pale grey (2·5 Y 5·5/0) on root channels, structure faces, and stones, some fine ochreous mottling (7·5 YR 5/8) especially on old roots and often between pale grey and olive-brown, clay loam to sandy clay; very weak cloddy.

MCF 3. *Locality*: Moses Cocker's Farm, Rivington. *Series*: Hallsworth. *Drainage of profile*: Very poor. *Drainage of site*: Receiving flush waters from higher slope. *Parent material*: Till of Carboniferous material. *Vegetation*: *Juncus*, *Deschampsia*, *Caespitosa*, &c.

Profile

2–½ in.	Brown F layer, felty, wet decomposing grasses, rushes, &c.; sharp boundary.
½–0 in.	Black amorphous H layer, seems to break easily to fine crumb, wet to very moist; sharp boundary.
0–1½ in.	Dull olive-grey (1 Y 3·5/1), silt loam with weak, very fine blocky structure; some roots; sharply defined boundary.
1½–10 in.	Dull grey (1 Y 4/1) with extremely abundant rusty (1·5 YR 3/5) coating on root channels and structure faces, silty clay loam to silty clay; fine to very small blocky well-defined structures; clearly defined boundary.
10–14 in.	Very pale grey (5 Y 6/2) with extremely numerous very dark brown concretions about 2 mm. in diameter, fairly hard (MnO_2?), silty clay; very weak and very fine prismatic to fine blocky; merging boundary.
14–25 in.	Pale grey (5 Y 6/2) with much MnO_2 (?) in larger cementations and some ochreous mottling (5·5 YR 5/8) on old roots, silty clay; very weak prismatic structure; merging boundary.
25–30 in.	Pale grey (5 Y 6/2), some olive-grey and olive-brown weathering sandstone and shale fragments, very pale grey on root channels with some ochreous mottling (5·5 YR 5/8), silty clay loam, rather weak prismatic structure; merging boundary.
30 in.+	Increasing proportion of olive-grey and olive-brown with some greenish-grey, very pale grey on root channels, some ochreous mottling on old roots (5·5 YR 5/8), increasing proportion of weathering shale giving tendency to laminated structure, silty clay loam.

TRACE-ELEMENT DISTRIBUTION IN SOME LANCASHIRE SOILS

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1. *Introduction*

In the years since W. O. Robinson published his comprehensive data on the inorganic content of some rarer elements in American soils (1914) the science of geochemistry has progressed considerably. Much more is now known about the distribution of the rarer elements in igneous and metamorphic rocks and their minerals, however, than in soils, and so long as sediments remain a relatively neglected body of rocks both from the petrological and geochemical points of view, pedologists will have only a vague idea of the amounts of minor elements likely to present themselves for soil formation in the very large areas where sedimentary rocks are the parent materials. The data in this paper, however, concern soils more than sediments although the initial approach was via underlying rocks.

TABLE 1

Lancashire Soils studied for Trace Elements

Parent material	*Drainage*	*Soil group*	*Soil series*	*Code*
Triassic drift	Imperfect	Meadow or Gley	Cottam	La 37/1–6
Triassic drift	Poor	Meadow or Gley	Salop	La 18/1–6
Carboniferous drift	Imperfect	Meadow or Gley	Rothwell	La 23/1–4
Carboniferous drift	Poor	Meadow or Gley	Hallsworth	La 41/1–5
Carboniferous drift	Very poor	Meadow or Gley	Gratrix	La 31/1–5
Carboniferous shale	Free	Brown Earth	Jepson	La 42/1–5
Carboniferous shale	Poor	Meadow or Gley	Hallsworth	La 26/1–6

Seven Lancashire soil profiles were studied (Table 1), three being developed on Carboniferous drift (i.e. boulder clay derived from Carboniferous material), two on Triassic drift, and two on Carboniferous shale. The only freely drained profile overlies Carboniferous shale; poorly drained profiles are represented on all the other parent materials; imperfectly drained profiles overlie both of the drift deposits and a very poorly drained profile is supported by the Carboniferous drift. Except for the freely drained soil which is classified as a Brown Earth, all the soils can be put in the Meadow or Gley soil group (showing different degrees of gleying according to the drainage).

In the field the soils formed on the Carboniferous and Triassic drifts are fairly easily distinguished, primarily on colour. Soils formed on mixed drift (derived from both Triassic and Carboniferous material),

however, are less readily distinguished, and it was thought that a knowledge of the trace-element contents of the pure drifts and their soils might assist the soil surveyor. Any outstanding differences between the latter soils could help in estimating the importance and distribution of the soils associated with the mixed drift. At the same time it was thought desirable to study the profile distribution of the minor elements in relation to drainage, and two profiles overlying Carboniferous shale, one being freely drained, were included.

2. *Experimental Procedure*

The air-dried soil (2–3 kg.) was sieved through a 2-mm. brass sieve and then successively quartered to give a portion of about 30 g. which was crushed with a porcelain pestle and mortar to 0·7 mm. diameter and sampled with a Perspex sampler to give about 4 g. This latter amount was finely ground with an agate pestle and mortar and samples taken therefrom were used for spectrographic analysis after heating at 450° C. for several hours.

(*a*) The determination of Co, Cr, Ga, Mn, Ni, Pb, Sn, and V followed the cathode-layer arc method of Scott (1946), Fe (the variable internal standard) being determined by the $\alpha\acute{\alpha}$ dipyridyl method. The line pairs used by Scott were also employed except for Mn 2,801·06 Å, Fe 2,838·12 Å and V 4,379·24 Å, Fe 4,250·79 Å; a Hilger large quartz spectrograph was used, and the range 4,500 Å to 2,750 Å was recorded on Kodak B 10 plates.

(*b*) La, Yt, and Zr were determined by comparing photometrically the intensities of the lines La 4,333·73 Å, Yt 3327·88 Å, and Zr 3,438·23Å produced on the cathode layer spectrogram (method (*a*) above) with those on spectrograms of standard mixtures recorded on Kodak B 10 plates of the same batch number and with identical excitation conditions.

(*c*) Boron was determined by using Sb as an internal standard and the line pair B 2,497·73 Å and Sb 2,598·06 Å (cf. Landergren, 1945). Copper electrodes 4 mm. in diameter and containing approximately 10 mg. of sample in a conical hole in the cathode were used for excitation; the middle 4 mm. of the 5-mm. arc column was focused on the collimator for 30 sec. with the current at 5 amps. Kodak B 10 plates were used.

(*d*) Ba, Li, Rb, and Sr were determined from an arc exposure recorded on two plates placed adjacent to each other in the plate holder; the electrodes and conditions were as in method (*a*) above. Cr, Cs (as the dichromate), and Sm (as the oxide) were used as internal standards and the following line pairs proved suitable: Ba 4,934·09 Å and Sm 4,815·81 Å; Li 6,707·84 Å and Cs 8,521·10 Å; Rb 7,800·23 Å and Cs 8,521·10 Å; Sr 4,607·33 Å and Cr 4,646·17 Å. Kodak II N plates 4 in. $\times 1\frac{3}{4}$ in. recorded the range 9,000 Å–5,800 Å; Kodak III J plates 4 in. $\times 2\frac{1}{2}$ in. recorded the range 5,800 Å–4,000 Å.

(*e*) The determination of Pb and Sn when below 40 p.p.m. in the sample was semi-quantitative, the method as used at the Macaulay Institute being followed (Mitchell, 1948*a*, p. 79), i.e. the arc was

TABLE 2

Iron and Minor Elements in a Poorly Drained Salop Series Profile formed on Triassic Drift

Sample number and depth from surface	*% loss on ignition (900° C.) on oven-dry basis (105° C.)*	*pH*	*Fe (%)*	*P.p.m. on oven-dry basis*														
				B	Ga	Cr	V	Sn	Li	Ni	Co	Zr	Mn	Yt	Sr	Pb	Ba	Rb	
La 18/1 0–4 in.	15·2	6·4	2·02	37	14	36	43	20	92	21	7·5	200	260	20	80	78	270	175	La 18/1
La 18/2 5–9 in.	5·5	5·2	2·38	—	20	38	48	8	98	21	10	240	220	38	77	52	430	165	La 18/2
La 18/3 11–15 in.	3·9	5·4	2·23	—	20	32	42	5	120	20	10	260	160	39	135	20	665	185	La 18/3
La 18/4 18–22 in.	3·9	5·7	3·35	—	30	61	70	—	145	26	10	280	230	26	85	15	540	235	La 18/4
La 18/5 24+in.	2·9	5·9	5·65	79	41	76	105	7	180	36	25	260	430	31	135	15	705	315	La 18/5
Sensitivity (Tables 2–5)				25	10	2	10	3	10	2	5	40	10	10	10	5	10	30	

Be (5 p.p.m.), Ge (10 p.p.m.), Mo (2 p.p.m.), Cu (10 p.p.m.), and La (80 p.p.m.) not detected; a dash (—) indicates absence of data.

focused on the slit and successive minutes of a 3-minute burn were photographed on Kodak B 10 plates.

The errors of the estimations are assessed as follows: Co, Cr, Ga, Mn, Ni, and V ±10 per cent. when more than 10 times the limit of sensitivity (see Table 2), otherwise ±40 per cent.; Ba, Rb, Sr, and Li ±15 per cent.; B ±20 per cent.; La, Yt, and Zr ±25 per cent.

3. *Discussion of the Data*

1. *Soils overlying drift*

Results for four of the profiles are tabulated in Tables 2–5 and it will be convenient to discuss initially those for the profiles overlying the Carboniferous and Triassic drifts. The data in Table 2 except for Mn and Zr are typical for the two soils overlying the Triassic drift (La 37/1–6 and La 18/1–5) and for two of the three soils overlying the Carboniferous drift (La 23/1–4 and La 31/1–5). There is a general tendency for the concentration of the elements Fe, Ga, Cr, V, Li, Ni, Co, Sr, Ba, and Rb to decrease from that in the lowest horizon as the profile is ascended and, moreover, the decrease occurs irrespective of the drainage conditions, which range from very poor through poor to imperfect. Semi-quantitative estimation showed that Mg likewise decreases with proximity to the surface and it is clear that overall leaching has been a powerful factor in the development of these profiles. The quantities of the above elements recorded for the lower soil horizons, although not readily matched collectively, are not individually unique for soils. Thus W. O. Robinson (1914), whilst reporting similar average amounts of Cr in three of his four groups of American soils and of V in one of the groups, recorded rather higher averages for Ba and much higher ones for Sr in two of the groups than found here in Lancashire; Mitchell (1944), in a study of the soils from north-east Scotland, gives concentration ranges for nine of the minor elements referred to above (i.e. excluding Fe) into which the values for the Lancashire soils fall and later (1948*b*) quotes figures for a Scottish soil overlying slate that compare closely with those for the five Lancashire soils overlying drift with the exception of Cr, which is somewhat higher in the Scottish soil, and Li, which is about three times as high in the English soils.

In the literature there is little referring to minor-element distribution in profiles of gleyed soils but there are numerous reports, to some extent conflicting, concerning grey-brown podzolic soils, which can be formed under climatic conditions fairly similar to those prevailing in Lancashire. Robinson's data (1914) show that Cr increases with depth in four such soils overlying very different parent materials (limestone, shale, sandstone, and granite), but the trends for V (which varies most from surface soil to subsoil), as well as for Ba, Sr, and Zr, are not constant. The data of Allison and Gaddum (1946) for some grey-brown podzolic soils in the United States show no consistent trend for Cr, V, Sr, or Ba in the profile, but indicate an increase of Co and Ni with depth. Slater *et al.* (1937) in American soils of a similar type found an increase of V and Ba with depth, but Cr fairly constant, and Ni varying

haphazardly. Malyuga (1944) in a study of the distribution of Co, Ni, and Cu in Russian soils demonstrated that Co and Ni were concentrated in the A_1 horizon of a leached grey forest soil (as they were also in the humus-rich horizons of other soil types), and Vinogradov and Bergmann (1949) showed that Cr tended to be concentrated in the B horizon of Russian grey forest soils whilst V remained sensibly constant. Pelisek (1940) remarked that Ba and Sr generally increased with depth in the hundred Moravian podzols he examined. The regular concentration changes for the elements seen in the Lancashire soil profiles could thus hardly have been predicted from published material.

Zr also tends to increase with depth in the Lancashire soils, but there is more of the element—certainly largely representing zircon—in the soils overlying Carboniferous drift (where Zr ranges from 260 p.p.m. to 600 p.p.m., and averages 440 p.p.m.) than in those overlying the Triassic drift (where Zr ranges from 200 p.p.m. to 350 p.p.m. and averages 275 p.p.m.). This confirms the findings of D. Mackney (personal communication) that zircon is more prominent in the heavy minerals of the soils on the Carboniferous than on the Triassic drift. (The percentages of heavy minerals were very similar.)

Mn is distributed most irregularly throughout the profiles although it is usually at a maximum in the C horizon; the contents of both drifts are comparable. Only a portion of the Mn in the parent material is present as the dioxide, but in the profiles dendritic MnO_2 is noticeable in the zones of oxidation, the higher values for Mn generally agreeing with the surveyors' notes on its relative occurrence. The lack of constancy of the ratio Fe/Mn throughout the profiles shows the marked difference in the behaviour of these elements; whereas Fe^{+3} is readily mobilized by reduction in gleying zones, MnO_2, once formed, is less easily reduced.

The profile distribution of Pb and Sn contrasts strongly with those for all the other elements studied; in every profile there is a marked and fairly regular increase in concentration from the lowest horizon to the surface, 160 p.p.m. Pb and 40 p.p.m. Sn (both in La 41/1) being the highest values found. It is possible that Sn is concentrated towards the surface due to its assimilation by plants, and the evidence of Pelisek (1942) that the upper layers of a podzol developed over a granite were enriched in Sn is relevant. However, he found Sn to increase fivefold from approximately 80 p.p.m. in the parent material, whereas in Lancashire soils the factor of increase may be up to 10 (La 41) and the parent material may contain as little as 3 p.p.m. Sn (La 23). From the results of Sinyakova (1945), who found that Pb generally increased with depth in Russian soils including forest soils, it is clear the Pb differs from Sn in that it is not concentrated by soil organic matter; the concentration factors here, although lower than those for Sn, may be up to seven (La 23). One source of the Pb is the barite present occasionally in concretions in some Lancashire soils (such a concretion supplied by D. Mackney contained several hundred p.p.m. Pb), but with the solubility of $PbSO_4$ exceeding that of $BaSO_4$ by about twenty times it would be necessary to suppose that the much less soluble PbS was formed in

order to save Pb from the downward-leaching fate experienced by Ba. It is, of course, possible that both Pb and Sn have been deposited from the atmosphere and that rain has had insufficient time to wash much of the metals down the profile. Nevertheless flue-dusts, for example, are not only rich in Pb and Sn, but contain often high quantities of Ga and Ge; Ga, although less variable in the profile than most of the other elements considered, tends to be concentrated with depth, whilst Ge was not detected (i.e. < 10 p.p.m.) in any of the samples.

The data for boron include determinations for the lowest horizon in which the values slightly exceed those at the surface; a number of authors have noted this trend for various soils including grey-brown podzolic soils (e.g. Tseitlin, 1939, and Hasler, 1942), whilst others have reported irregular trends for similar soils (e.g. Whetstone *et al.*, 1942). The values recorded here, ranging from about 35 to 80 p.p.m. boron, are of the order expected.

Soil profile La 41 (Table 3) shows interesting features in the field for a gley soil (Crompton, 1952); whereas the top 9 in. are dark grey with moderate rusty mottling on root channels, the next 3 in. are dull light grey and there is a clear boundary between this and a bright orange-yellow horizon underneath extending from 12 in. to 24 in. from the surface. The horizon 9 in. to 12 in. has been fairly strongly bleached, as the figures for the Fe contents of portions of the horizons (Table 3) show. Below the iron-poor horizon there is a fivefold increase of Fe and the value there (5 per cent.) exceeds that for the parent material (4 per cent.), recalling the distribution of Fe in podzolized profiles. The ratio of three to one for Fe in the surface (1 in. to 5 in.) to Fe in the bleached (10 in. to 12 in.) horizon, however, is unreasonably high for a podzol (see, for example, Muir, 1934, and Joffe, 1949) and the existence of strong mottling in the profile is a proof of gleying. The minor elements Ga, Cr, Ni, Co, and Mn are less than half as abundant in the bleached layer than in that sampled below, but the ratio element:Fe is only approximately constant for Ni (and, possibly, Co); V and Sr are but slightly lower in the bleached layer and they are evidently less easily mobilized by the solutions that so drastically removed the Fe. The profile trends for the other minor elements studied are not much disturbed by the Fe-poor layer, and in particular Sn and Pb increase fairly regularly from the lowest horizon to the surface.

Of the minor elements B, Ga, Cr, V, Sn, Li, Ni, Co, Zr, Mn, Yt, Sr, Pb, Ba, and Rb present in the Triassic and Carboniferous drifts and five overlying soils, only Zr is significantly different in concentration in the two groups to enable a distinction to be made; this merely implies that the zircon contents of the two drifts are dissimilar, being higher in the Carboniferous drift. Lanthanum is detectable only in profile La 23 (Carboniferous drift), but the concentration (100 p.p.m. throughout) is only slightly above the sensitivity (80 p.p.m.), and no general conclusion can be drawn. Rough estimates of the relative amounts of Ca, Na, Mg, and Ti in the soils and parent materials show that Mg is appreciably higher in the Triassic drift and soils; the other elements have similar concentrations.

TABLE 3

Iron and Minor Elements in a Poorly Drained Hallsworth Series Profile formed on Carboniferous Drift

Sample number and depth from surface	*% loss on ignition (900° C.) on oven-dry basis (105° C.)*	*pH*	*Fe (%)*	*P.p.m. on oven-dry basis*														
				B	Ga	Cr	V	Sn	Li	Ni	Co	Zr	Mn	Yt	Sr	Pb	Ba	Rb	
La 41/1 1–5 in.	17·9	6·6	3·19	58	29	35	63	40	130	14	10	300	530	19	85	160	780	140	La 41/1
La 41/2 10–12 in.	6·8	6·5	0·95	—	22	24	45	20	140	4·2	*	260	52	33	91	35	420	145	La 41/2
La 41/3 14–18 in.	6·4	6·6	4·99	—	45	50	76	7	120	17	10	310	140	29	130	45	535	180	La 41/3
La 41/4 26–30 in.	4·6	6·4	3·27	—	24	48	67	8	135	19	10	345	190	43	69	20	535	170	La 41/4
La 41/5 38–42 in.	4·0	5·6	4·06	66	31	58	63	4	105	21	20	510	450	19	93	25	435	165	La 41/5

Be (5 p.p.m.), Ge (10 p.p.m.), Mo (2 p.p.m.), Cu (10 p.p.m.), and La (80 p.p.m.) not detected; a dash (—) indicates absence of data and an asterisk (*) indicates Co below sensitivity (5 p.p.m.)

4. *Soils overlying Carboniferous Shale*

The two profiles overlying shale of approximately Millstone Grit age are quite dissimilar, due not to the drainage differences but to the compositions of the parent materials.

Profile La 42/1–5 is freely drained and can be classified as a Brown Earth (contrasting with all the other soils, which are gleyed); the elements Ga, Cr, V, Li, Ni, Ba, and Rb are again, however, concentrated with depth in the profile (Table 4) and the degree of enrichment is of the same order as for the gley soils. The soil was re-seeded in 1948 to give a permanent pasture (when sampled in 1951) and lime has been applied; this is reflected in the high Ca and distinctly high pH of the top horizon (compared with those below it) and in the distribution of Sr. The anticipated trend of Sr increasing with depth is disturbed by the addition of Sr always contained as a trace element in lime, and the concentration of the element is maximal at the extremes of the profile. Sn and Pb are markedly concentrated towards the surface; the relative increase of Sn compares closely with those found in the other profiles, but Pb is less concentrated at the surface in the Brown Earth than in the Gley soils. A partial explanation may be that the very insoluble lead sulphide has little chance to form in the freely drained profile and the portion of Pb present as the sulphate is, like Ba, leached out and washed downwards. The minor-element concentrations in this Brown-Earth profile are very similar to those shown for the profiles overlying Carboniferous drift (e.g. Table 3, lower horizons) except for Pb in the C horizon. (Zr is higher than in the profiles overlying Triassic drift.) The similarity is, nevertheless, fortuitous (see below) and cannot be taken to suggest that shale from this locality gave rise during Quaternary times to the Carboniferous drift; the shale may vary in the field from arenaceous to argillaceous and an average composition would be difficult to assess. The Carboniferous shale and overlying profile La 26/1–6 have Fe and minor-element contents (Table 5) markedly different from those in profile La 42/1–5. Fe is two or more per cent. higher, Mn up to 1,000 p.p.m. higher, and Cr, Sn, and Co slightly higher; Zr is even lower than in the Triassic drift. On these analytical data no horizon could be confused with any of the soil horizons overlying the Carboniferous or Triassic drifts. The behaviour of the elements is, however, very similar in this poorly drained profile to that shown by the other gleyed profiles, viz. there is a general decrease of concentration from the parent material upwards for the elements Ga, Cr, V, Li, Ni, Co, Yt, Sr, Ba, and Rb, and a decrease with depth of Sn and Pb; Mn is again rather irregularly distributed in the profile.

5. *Conclusions and Summary*

In all the six Lancashire gleyed soils supporting permanent pasture, the maximum concentration of the elements Fe, Ga, Cr, V, Li, Ni, Co, Zr, Yt, Sr, Ba, and Rb occurs in the lowest horizon. Generally there is a fairly regular decrease in the abundance of these elements as the profile is ascended (oven-dry basis), and the degree of impoverishment

TABLE 4

Iron and Minor Elements in a Freely Drained Jepson Series Profile formed on Carboniferous Shale

Sample number and depth from surface	*% loss on ignition (900° C.) on oven-dry basis (105° C.)*	*pH*	*Fe (%)*	*P.p.m. on oven-dry basis*														
				B	Ga	Cr	V	Sn	Li	Ni	Co	Zr	Mn	Yt	Sr	Pb	Ba	Rb
La 42/1 0–5 in.	14·0	7·9	2·94	58	19	32	40	30	100	23	10	270	400	26	120	78	300	185
La 42/2 7–11 in.	6·8	5·8	3·18	—	20	40	46	25	100	24	15	300	630	35	100	35	390	180
La 42/3 13–17 in.	6·0	5·2	3·24	—	25	41	47	20	150	17	10	420	410	34	110	45	310	350
La 42/4 19–23 in.	5·2	5·4	3·64	—	27	55	59	10	130	35	20	400	345	35	100	45	670	240
La 42/5 24–27 in.	4·3	5·2	3·89	66	31	66	64	10	110	44	20	400	260	35	125	40	545	285

Sample number and depth from surface
La 42/1
La 42/2
La 42/3
La 42/4
La 42/5

Be (5 p.p.m.), Ge (10 p.p.m.), Mo (2 p.p.m.), Cu (10 p.p.m.), and La (80 p.p.m.) not detected; a dash (—) indicates absence of data.

TABLE 5

Iron and Minor Elements in a Poorly Drained Hallsworth Series Profile formed on Carboniferous Shale

Sample number and depth from surface	*% loss on ignition (900° C.) on oven-dry basis (105° C.)*	*pH*	*Fe (%)*	*P.p.m. on oven-dry basis*														
				B	Ga	Cr	V	Sn	Li	Ni	Co	Zr	Mn	Yt	Sr	Pb	Ba	Rb
La 26/1 1–5 in.	16·5	5·0	4·36	62	22	51	60	35	140	22	25	150	1,200	10	64	100	530	190
La 26/2 6–10 in.	11·9	5·1	4·76	—	42	67	75	25	150	22	25	200	1,400	15	62	115	590	190
La 26/3 11–15 in.	12·1	5·2	5·46	—	49	84	67	15	175	28	30	150	1,750	15	53	25	690	165
La 26/4 16–20 in.	9·3	5·1	7·07	—	52	103	99	12	180	40	30	150	1,500	16	57	15	780	200
La 26/5 21–24 in.	9·1	4·5	7·72	—	52	104	94	12	190	42	25	110	1,100	18	67	20	760	250
La 26/6 24+ in.	8·4	4·7	6·70	34	50	94	90	15	180	45	30	190	1,300	21	58	20	960	220

Sample number and depth from surface
La 26/1
La 26/2
La 26/3
La 26/4
La 26/5
La 26/6

Be (5 p.p.m.), Ge (10 p.p.m.), Mo (2 p.p.m.), Cu (10 p.p.m.), and La (80 p.p.m.) not detected; a dash (—) indicates absence of data.

is independent of the drainage conditions (imperfect, poor, and very poor). The Brown-Earth profile examined shows the same relative distribution for the above elements with the exception of Sr. The working of the land prior to the re-seeding in 1948 and the freely drained nature of the profile have not resulted in a higher degree of overall leaching than in the gleyed soils; the addition of lime has not affected the soil reaction below the surface horizon which, like all the other horizons in this and the six gleyed soils studied, is slightly acid. Sr, however, being contained in the lime, is as abundant in the surface soil as in the parent material. All the soils show Sn and Pb concentrated in the surface layers. It is suggested that Sn here may be concentrated in organic matter (as found by others) which increases towards the surface. Pb is a trace element in the barite associated with some Lancashire soils; its break with Ba in weathering may be due to the formation of the very insoluble sulphide PbS and the preferential leaching of the more soluble $BaSO_4$. The absence of Ge (below 10 p.p.m.) and the behaviour of Ga in increasing with depth suggest that Sn and Pb are not derived from the atmosphere. The only element which has an irregular distribution in the soil profiles is Mn; the formation of the dioxide renders Mn relatively immobile—more so than ferric hydroxides—and leaching and gleying processes are not easily able to redistribute it.

The two drifts underlying soil profiles can be distinguished by their Zr contents. Zircon, accounting for most of the Zr, is higher in the Carboniferous drift, and mineralogical studies in the abundance of this mineral would suffice to decide whether a mixed drift was derived from predominantly Triassic or Carboniferous material. Since the total concentrations of the other minor elements studied are similar in both the drifts and their soils, they are of no diagnostic value to the soil surveyor; the available concentrations may, however, be dissimilar and useful, as future work will decide.

The minor-element concentration differences in the two Upper Carboniferous shales and their soils show the variability of the parent material. Values for one of the profiles (La 42/1–5) are virtually the same as those for profiles La 23/1–4 and La 30/1–5 overlying Carboniferous drift; those for the other profile are unique in the seven profiles studied.

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FREE IRON-OXIDE REMOVAL FROM SOILS

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THE removal and determination of the free iron oxide* associated with soils is particularly difficult, as many minerals of secondary origin, e.g. ferriferous aluminosilicates in the clay fraction, are very susceptible to attack at low pH values. The use of acids is therefore precluded, and methods applicable in the range pH 3·25–7·0 are normally employed.

Most available methods (see e.g. Dion, 1944; Jeffries, 1945; Roberts, 1947; Deb, 1949) employ reducing or complex-forming organic reagents, but since these have to be destroyed before using the colorimetric sodium-salicylate method (Scott, 1941) for iron determination (that normally employed here), a completely inorganic procedure would be of considerable use for routine estimations. The only methods of this type hitherto proposed employ hydrogen sulphide (Drosdorff, 1941; Drosdorff and Truog, 1935; Toth, 1937), sodium bisulphite (Brammall and Leech, 1940), or sodium hydrosulphite (Galabutskaya and Govorova, 1934). However, since methods employing hydrogen sulphide were considered unsuitable because of the somewhat objectionable nature of this compound in the laboratory, and since the sodium bisulphite method was found, after examination, to be very inefficient, only the sodium hydrosulphite procedure seemed worthy of further study. A modification of this method has recently been employed by Deb (1950), but, as he introduced organic reagents, only the applicability and effectiveness of the method in essentially its original inorganic form is examined here.

As only scanty information regarding the original technique was available,† preliminary experiments were performed to determine the optimum conditions for iron removal with minimum decomposition of the clay minerals. These conditions were satisfied using two extractions with 4 per cent. sodium hydrosulphite solution of pH 5·8, with intermediate and final washings with 0·05 N. hydrochloric acid (Mitchell and Mackenzie, 1954). Since very little, if any, clay-mineral decomposition occurred at pH 3·5 (the pH of a solution of sodium hydrosulphite in water), it was considered that this modification of the method, which is more rapid and obviates pH adjustment, might be applicable as a routine method for soils, where any *very slight* decomposition would be expected to have no appreciable effect upon the final result—at least in so far as the amount of iron is concerned. Consequently, two modifications of the method were tested with soils (*a*) without pH adjustment and (*b*) with pH adjustment of the sodium-hydrosulphite solution. Full details are

* The term *free iron oxide* is used here to include all iron not present in the crystal lattice of any component mineral, excepting, of course, the iron oxide minerals themselves.

† As the original paper was unobtainable in this country, only the information contained in an abstract was available.

given below, and the results obtained are discussed and compared with those given by the acid ammonium-oxalate method of Tamm (1922) and the aluminium-ammonium-tartrate method of Dion (1944).

Experimental

Method (*a*). Into a 50-ml. centrifuge tube are carefully weighed out 2·00 g. of air-dried < 2 mm. soil, 5–10 ml. distilled water added, and the centrifuge tube immersed in boiling water for 20 minutes (see Note 1). Into a *dry* 100-ml. measuring cylinder are weighed out 2 g. (±0·02 g.) sodium hydrosulphite (commercial grade—*c.* 50 per cent. $Na_2S_2O_4$), 50 ml. distilled water added, and the salt dissolved by shaking (see Note 2). To the soil suspension 40 ml. of this solution are *immediately* added, and the centrifuge tube is immersed in water at 40–45° C. for 5 minutes with occasional shaking; the suspension is then centrifuged and the supernatant liquid collected in a 250-ml. beaker (beaker 1) (see Note 3). To the centrifuge tube 50 ml. of 0·05 N. hydrochloric acid are then added, the soil residue redispersed by shaking, and the tube immersed in water at 40° C. for 3 minutes with occasional shaking; the suspension is recentrifuged and the clear extract collected in a 400-ml. beaker (beaker 2). The treatments with sodium hydrosulphite and with hydrochloric acid are repeated in exactly the same manner, the hydrosulphite extract being added to beaker 1, and the hydrochloric acid extract to beaker 2. In order to remove soluble iron salts retained in the soil, two washings are given with neutral N. sodium chloride, these washings being added to the extracts in beaker 2.

Method (*b*). The procedure is identical with that for method (*a*), except that the sodium hydrosulphite instead of being dissolved in water is dissolved in a sodium-hydroxide solution of such strength as to give the resulting hydrosulphite solution a pH of about 6·5. The requisite strength of sodium hydroxide is predetermined; the system is somewhat buffered over the range pH 5·6–7·5 so that small variations in the amount of sodium hydroxide do not alter the pH by any great amount. For the sodium hydrosulphite used here, solution of 2 g. in 50 ml. of approximately 0·3 per cent. sodium hydroxide was found to give the requisite pH. Using such a solution, the time of extraction should be increased to about 10 minutes.

Determination of iron. The beakers 1 and 2 are covered and heated on the steam-bath for 20–30 minutes (see Note 4); 40–50 ml. of 20 volume A.R. hydrogen peroxide (see Note 5) are added, 10 ml. at a time, to beaker 1 and 15 ml. to beaker 2; 10 drops concentrated hydrochloric acid are also added to beaker 2 (see Note 6), and the solutions reheated until effervescence ceases. The cover-glasses are removed, the solutions evaporated to a reasonable volume, combined, evaporated again, if necessary, and filtered through an 11-cm. Whatman No. 30 filter-paper into a volumetric flask of capacity depending upon the amount of iron anticipated. This can be roughly estimated from the intensity of the yellow colour of the solution, approximate dilutions being: < 0·3 per cent., 250 ml.; 0·3–1·5 per cent., 500 ml.; > 1·5 per

cent. 1,000 ml. A suitable aliquot (2–20 ml.) is then used for iron determination by the salicylate method of Scott (1941).

Alumina may also be determined in this extract by the colorimetric aluminon method of Robertson (1950).

Notes

1. Thorough wetting before treatment with sodium hydrosulphite is essential to avoid the formation of black insoluble iron compounds.

2. Because of its instability in solution, it is essential that the sodium hydrosulphite solution be made up *fresh* for *each* soil; use of a *dry* 100-ml. cylinder ensures the minimum amount of decomposition before the solution is added to the soil. This part of the procedure should be performed as rapidly as possible.

3. It is preferable to keep separate the sodium hydrosulphite and the acid extracts, as otherwise heavy deposition of sulphur is liable to occur.

4. Addition of hydrogen peroxide to the cold solutions causes, on heating, a heavy deposition of sulphur, which is not readily oxidized. When added slowly to hot solutions, however, most of the sulphur which precipitates is oxidized on further heating, and the remainder coagulates to form lumps which are easily filtered off. If the hydrogen peroxide were added sufficiently slowly, it is possible no sulphur would be precipitated.

5. It is essential to use A.R. grade hydrogen peroxide (AnalaR was actually used in these experiments), as the B.P. grade contains inhibitors which make it very inefficient for this application (see Mitchell and Mackenzie, 1954).

6. Any organic matter removed from peaty soils is readily oxidized by the hydrogen peroxide and consequently does not interfere with the determination.

7. With peaty soils, addition of hydrogen peroxide to the hydrochloric acid-sodium chloride extract sometimes causes precipitation of some iron as (presumably) $Fe(OH)_3$. To prevent this 20 drops (1 ml.) of concentrated hydrochloric acid should be added to this extract before the peroxide, instead of the 10 drops added as a precautionary measure to normal soils (see text).

Results and Discussion

During the initial stages of development of the method, a filtration technique, similar to that described for the original method (Galabutskaya and Govorova, 1934), was compared with the centrifuge technique described above. Because the rate of filtration is generally very slow, however, this process was found to be very time-consuming without appreciably better iron removal (e.g. 0·51 per cent. compared with 0·49 per cent.), while the long time of contact would tend to increase the danger of serious attack upon the component minerals. For these reasons it seemed preferable to adhere to the centrifuge procedure, and this has, in fact, proved most convenient.

Preliminary tests with clays indicated that while two treatments with sodium-hydrosulphite solution were necessary for reasonably complete removal of all the free iron oxide, a third treatment removed very little; in addition, one prolonged treatment was not nearly so effective as two separate treatments with an intermediate acid wash (see Mitchell and Mackenzie, 1954). For soils, the results in Table 1, which includes for comparison free iron-oxide percentages as determined by the method of Tamm (1922), clearly demonstrate the necessity for two treatments, and also that both modifications of the method are about equally effective. The soils used cover a large range of different soil types and of free iron-oxide contents.

TABLE 1

Amounts of Free Iron Oxide removed from Soils by Various Treatments

Soil	% Fe_2O_3 *removed by:*				
	Acid oxalate method	*Method (a)*		*Method (b)*	
		Single treatment	*Double treatment*	*Single treatment*	*Double treatment*
24953A	4·88	4·45	4·83	3·83	5·07
54548	1·87	1·63	1·79	1·47	1·72
47347	1·24	2·05	..	..	2·70
30220	0·46	0·77	1·03	0·70	1·00
48099	0·37	0·49	..	0·49	..
30257	0·08	0·12	0·14	0·09	0·12

Since no care has to be exercised in adjusting pH, method (*a*) is the most convenient experimentally, and it was used to investigate a further range of diverse soil types. The results, as compared with those obtained by the acid ammonium-oxalate extraction and the aluminium-ammonium-tartrate digestion, are given in Table 2. For the hydrosulphite and acid ammonium-oxalate methods the extracts were analysed for aluminium and comparable figures are entered in the table; the aluminium-ammonium-tartrate extracts were not analysed for this element.

Generally, the amounts of free iron oxide as determined by the hydrosulphite method are somewhat higher than those determined by the other two, and, on the whole, cleaner products were obtained. In addition, duplicate extractions gave very consistent results. The relative trends down any particular profile remain essentially the same irrespective of the method used, but since it is known that the acid ammonium-oxalate technique does not give complete removal in the absence of sunlight (Deb, 1950), the values obtained by it would be expected to be less than the true amounts of iron oxide present. Similarly, the aluminium-ammonium-tartrate method has been found inefficient for some of our soils, so it appears that the hydrosulphite procedure gives more nearly the actual amounts. As regards alumina, only about half that extracted by acid ammonium oxalate is removed by hydrosulphite, which is not surprising in view of the different action of the two reagents. However, it is worthy of note that the trends down the profile are again the same with both reagents, in spite of incomplete removal with sodium hydrosulphite.

The method as finally adopted, therefore (method (*a*)), is fairly rapid. Two sets of four determinations (or more, depending upon the capacity of the centrifuge) can be performed per day, the treatment on the steam-bath requires little attention, and one half-day is ample for final volume adjustment and the colorimetric iron determination of 12 or 16 samples. No complex arrangements are necessary for destruction of organic matter, and in addition, the results, as well as the colours of treated soils, indicate fairly complete, if not entirely complete, removal of the free iron oxides. While removal of alumina is not so satisfactory, the

method can apparently give valid information upon trends down a profile.

The author desires to express his thanks to Miss K. R. Farquharson, who performed the aluminium-ammonium-tartrate digestions.

TABLE 2

Amounts of Sesquioxides removed from Typical Profiles by Various Treatments

Soil	Location and series	% Fe_2O_3 removed by			% Al_2O_3 removed by	
		Tamm's method	*Dion's method*	$Na_2S_2O_4$ *method*	*Tamm's method*	$Na_2S_2O_4$ *method*
48119	Hill of Fare	0·10	0·12	0·12, 0·14	0·07	0·05
48120	(Podzol)	0·15	..	0·20, 0·22; 0·21	0·35	0·155; 0·14
48121		0·17	0·21	0·36; 0·33	0·23	0·13; 0·135
48122		2·60	2·24	2·85, 2·95	1·91	0·78
48123		2·78	2·70	2·96, 2·98	2·66	1·24
48124		1·26	1·12	1·35	3·48	1·65
48125		0·60	0·50	0·60	1·02	0·71
30218	Ythanwells	1·69	1·76	1·96	0·93	0·58
30219	(Shallow,	1·97	1·70	2·54	1·60	1·00
30220	well-drained)	0·46	0·59	1·08	0·83	0·68
30221		0·52	0·93	1·27	0·95	0·71
30222	Ythanwells	0·83	0·88	1.00, 0·97	0·52	0·29
30223	(Poorly drained)	0·32	0·70	0·76	0·25	0·20
30224		1·02	1·09	1·60	0·26	0·33
30225		0·55	0·88	1·52	0·22	0·29
40978	Tillycorthie	1·52	1·77	1·97, 2·01; 1·94	0·80	0·59; 0·66
40979	(Well-drained)	0·66	1·20	1·31, 1·25	0·75	0·50
40980		0·59	0·58	1·34, 1·29	0·58	0·49
40981		0·59	0·64	1·18, 1·16	0·54	0·47
30258	Windyhills (Iron pan)	4·93	5·28	5·88, 5·97	1·12	0·71
47350	Balquhain (Very poorly drained)	2·17	..	2·50, 2·58	0·66	0·38

Results, in columns 5 and 7, separated by commas, represent duplicate determinations on aliquots of the same solution; those separated by semi-colons indicate duplicate results for separate extracts.

Summary

A completely inorganic technique very convenient for routine determinations of the amount of free iron oxide in soils is described. Two modifications of the method were tested, and that eventually chosen is compared with other available methods, especially as regards its efficiency in removing both Fe_2O_3 and Al_2O_3.

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